



THE UNIVERSITY *of* EDINBURGH

Edinburgh Research Explorer

Experimental study of thickening effectiveness of two herders for in-situ burning of crude oils on water

Citation for published version:

Rojas Alva, U, Fritt-Rasmussen, J & Jomaas, G 2020, 'Experimental study of thickening effectiveness of two herders for in-situ burning of crude oils on water', *Cold Regions Science and Technology*.
<https://doi.org/10.1016/j.coldregions.2020.103083>

Digital Object Identifier (DOI):

[10.1016/j.coldregions.2020.103083](https://doi.org/10.1016/j.coldregions.2020.103083)

Link:

[Link to publication record in Edinburgh Research Explorer](#)

Document Version:

Peer reviewed version

Published In:

Cold Regions Science and Technology

General rights

Copyright for the publications made accessible via the Edinburgh Research Explorer is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy

The University of Edinburgh has made every reasonable effort to ensure that Edinburgh Research Explorer content complies with UK legislation. If you believe that the public display of this file breaches copyright please contact openaccess@ed.ac.uk providing details, and we will remove access to the work immediately and investigate your claim.



Experimental study of thickening effectiveness of two herders for in-situ burning of crude oils on water

Ulises Rojas Alva^{a, b}, Janne Fritt-Rasmussen^c, Grunde Jomaas^{a, b}

^aDepartment of Civil Engineering, Technical University of Denmark, Kgs. Lyngby. 2800-Denmark

^bSchool of Engineering, BRE Centre for Fire Safety Engineering, University of Edinburgh, EH9 3FG, United Kingdom

^cDepartment of Bioscience, Aarhus University, Frederiksborgvej 399, 4000 Roskilde, Denmark

Abstract

The thickening effectiveness of two commercially available herding agents (OP40 and TS6535) was investigated parametrically in small-scale laboratory experiments with two different crude oils (ANS - Alaska North Slope and Grane). Both fresh and emulsified in cold water conditions were used in order to provide further information for in-situ burning operations in an Arctic context. Two application procedures for the herder, as well as variations in the duration of the tests, were other variations in the study. Both herding agents demonstrated the ability to obtain the minimum oil slick thickness (1-5 mm) required for successful in-situ burning. OP40 was more efficient for short periods than TS6535, whereas TS6535 remained active for long periods (up to 400 hours). Both herders were more efficient in pre-spill application than post-spill application of the herder. The herder monolayer was not affected during burning and was still active once the burning ceased. Nonetheless, some contradictory results were found over a range of parameters, but are still in line with previously reported findings. Further systematic studies study based on physical/chemical characteristics of the oils and herders are required to fully establish the physical dependencies.

Keywords: oil spills, herding agents, thickening effectiveness, in-situ burning

1. INTRODUCTION

One of the techniques for oil spill response in open waters and ice-infested waters is igniting and burning the oil; also referred to as in-situ burning (ISB) [1–4]. In-situ burning has demonstrated the potential to be a fast method to remove substantial amounts of oil, and previous tests (under particular conditions such as calm seas, winds bellows 10 m/s, and relatively low weathering degree of the oil) have yielded very high burning efficiencies (BE) up to 95% [3–11]. For example, 411 individual burns took place during the Deepwater Horizon oil spill in the Gulf of Mexico [12,13]. However, the ISB method entails various challenges with respect to efficient application. One key challenge is that crude oil spreads when it is spilled on water, and the thickness of the oil slick can become too thin to be ignited (due to the heat losses to the underlying waterbed). If the oil slick is thick enough, the thermal losses are reduced sufficiently for the oil slick to be ignited, and self-sustained burning can be achieved. Therefore, a minimum oil slick thickness is one of the requirements for successful ISB. Previous investigations have found that the minimum oil slick thickness for successful ISB is between 1-2 mm and 2-5 mm for fresh crude oils and weathered crude oils, respectively [1,14–18].

The oil slick can be thickened by two means, either mechanically or chemically. The mechanical confinement is achieved by using fire-resistant booms that are deployed and operated by vessels in the open water or up to ~3/10 ice cover [1]. However, the efficiency of the ISB method can be affected by large concentrations of ice, and in the worst case, it will not be a possible mitigation method because the fire-resistant booms cannot be used under such circumstances [1,2].

The second way of thickening an oil slick is by use of chemicals that are also known as herding agents. The herding agents are applied around the spilled oil slick and rapidly forms a monomolecular layer. Due to the high spreading pressure of this monomolecular layer, the surface tension of the water is reduced from approximately 70 mN/m to 20-30 mN/m [1,19,20]. When this monomolecular layer reaches the oil slick edges (oil has spreading pressures in the range of 10 to 20 mN/m), the oil is contracted, resulting in a much thicker oil layer owing to the equilibrium of interfacial forces [1,4,21]. Currently, only two herding agents are listed in the U.S. Environmental Protection Agency NCP Product Schedule [22]. The first is the U.S. Navy cold-water herder formulation formerly known as USN and most recently renamed ThickSlick 6535 (TS6535), while the other is the silicone-based herder OP40, previously known as Silsurf A004-UP [23].

Another major challenge for successful ISB is related to the weathering process that crude oils undergo once released on the sea surface. Evaporation and emulsification are the most relevant weathering processes. During evaporation, the lighter compounds of the oil evaporate [24]. The evaporation process precipitates the most polar and most condensed asphaltenes and resins in the oil. Then, the residual oil mixes with seawater (due to wave energy) and the water droplets will remain embedded due to the presence of surfactant-like agents (asphaltenes and resins) [25]. As a consequence, the viscosity and volume of oil increase dramatically [24,26], and this also leads to changes in the surface tension of the oil [27,28], all of which are challenging the successful use of herders.

Despite these known challenges, only a few studies have been undertaken with herders and weathered crude oils [29–33]. These experiments were conducted across a range of test scales (in laboratory conditions and in the outdoors), as well as in the field. Both herders performed better on weathered crude oils than on fresh oils [29–31]. On fresh ANS and Grane, OP40

performed better than TS6535 [29–31,34,35]. However, Potter and co-workers [30] found that TS6545 performed similarly or better than OP40 on evaporated ANS.

From the existing studies, various parameters were selected to determine their respective effect on the herding process for ISB. Besides weathering, other parameters (some not studied to a great extent) include oil types, salinity in the water, water temperature, air temperature, wind, waves, ice presence, ice type, test duration, oil sheens, herder application (post or previous to the oil application) and oil volume. Figure 1 provides an overview of the previous studies as a function of the herder agents and the experimental rig size, and shows how the current work is complementary.

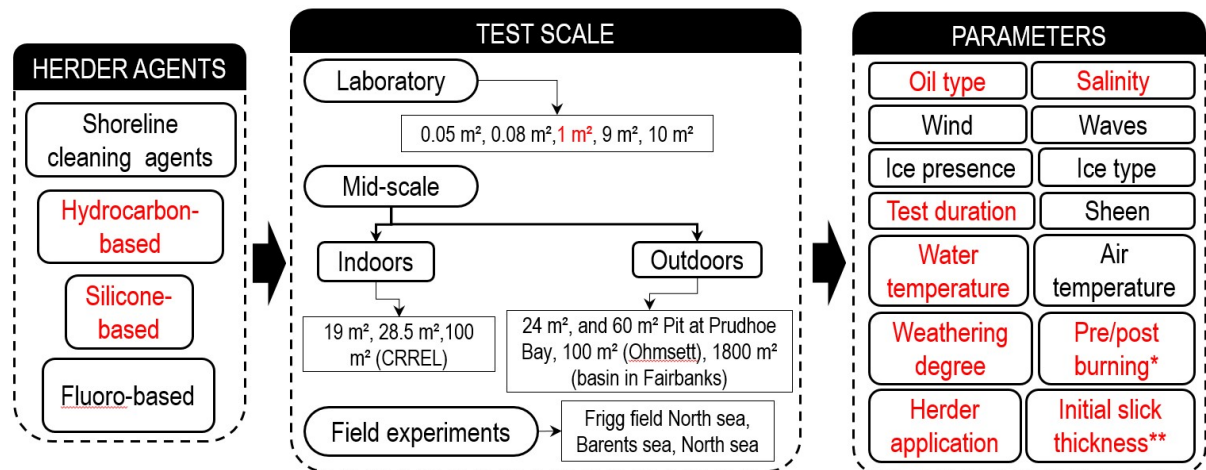


Figure 1 – Chart of experimental parameters of all previous studies in the literature where the herder effectiveness was investigated. The text in red represents the parameters studied herein. *)The pre/post burning parameter, where the herder behavior was analysed during and after burning, was only studied in the current study. **) The initial slick thickness was not specifically studied as a parameter in literature, nor in the current study, but was analysed.

The water temperature and water salinity have been reported to have contradictory results on both herders [4,21,29,30,34–37]. The pre-spill application showed that both herders are more efficient in holding thicker oil thicknesses than post-spill application [4,33]. The efficiency of both herders can also be defined as a function of the thickening duration. OP40 was reported to decline after one hour whereas TS6535 maintained its properties for a longer time (up to 6 hours) [4,21,29,35,37]. Some of the results from the literature (see Figure B. 2 to Figure B. 5 in APPENDIX A) shows a dependency as a function of the initial oil thickness (or oil amount tested) [4,21,29–31]. Also, the results across various rig scales in laboratory conditions, in the outdoors and in the field can vary substantially [4,21,30–32,37,38].

Even though it is important to evaluate whether the herder is still active after burning, the consequences of the ISB process on the herding agent are not known. It has been reported that the oil slick undergoes a dynamic process where it expands and contracts during ISB with herder as confinement [14,20,33,39] ([33] and [39](accepted)). If the oil slick expands during burning, the oil slick thickness reduces, thereby increasing the heat losses towards the water bed. As a consequence, the BE results in chemically herded slicks can be expected to be lower than in experiments with physical confinement (with fire-resistant booms) [39].

Guided by the previous studies and the knowledge gaps shown in Figure 1 (weathering, oil type, test duration, herder application, water salinity, initial oil slick thickness, and herder

performance during and after burning), the current experimental study investigated the thickening effectiveness of two herding agents on two crude oils. The herding agents were OP40 and TS6535, and the crude oils were Alaska North Slope (ANS) and Grane and their corresponding artificially weathered emulsion (with 25% water content). Several small-scale tests were carried out in a 1 m² water basin in calm conditions, and the water temperature and salinity mimicked Arctic conditions in most of the experiments (in others non-saline tap water was used). In addition, other parameters were explored such as various durations, application procedures (application of the herding agent before and after the oil) and during and after combustion. It should be noted that the current study is complimentary of two other investigations: (1) The burning behaviour of the crude oils and (2) the studies of environmental effects of the herding [31,39,40]. Hence, some experimental aspects of this study were partly constrained by the experiments of the complementary investigations.

In summary, the goal of the current experimental study was to carry out a systematic parametric study of the use of herders for in-situ burning in order to provide results that can guide the use in the field. In other words, it provides further insight into the validity of the ISB method with herders for a range of parameters such as oil type, herder type and weathering processes. In addition, the study identified key areas that require further research.

2. EXPERIMENTAL SET-UP AND METHODOLOGY

The methodology employed in the experimental study is presented and discussed in this chapter across various sections.

2.1 The crude oils and herding agents included in the study

Two crude oils were selected for this study; Grane and Alaska North Slope (ANS) and their corresponding 25% water-in-oil emulsions. Grane is an asphaltenic crude oil with a high content of resins [15] from the North Sea, Norway. ANS is a medium grade crude oil, with lower density and viscosity than Grane, from the Alaska North Slope region, Alaska, USA.

The 25% water-in-oil emulsion for each oil was artificially made by a modified version of the rotating flask technique [41]. The technique is explained in detail by Daling et al. (2003) [25], and it has been used in previous studies [15,30,42]. It has been claimed that this rotating flask technique creates less stable and not representative emulsions compared to other methods [43]. For this study, however, the objective was to create ignitable emulsions in order to evaluate their burning behaviour for a complementary study [39]. The onset and formation of emulsions depend on various factors, such as the content of high polar asphaltenes and wax components in the oil, the weathering conditions (wind, waves, and temperature), the climatological conditions, and the oceanic conditions. The stability of the emulsion also depends on the water content [44,45], which influences the ignitability of the weathered oil because the water droplets need to be separated from the oil to achieve sustained burning. Previous studies have shown that as the emulsion becomes more stable with higher water content, the weathered crude oil is less likely to ignite and achieve sustained burning [3]. The stability degree of an emulsion can significantly influence the ignitability of the emulsion. A strongly stable emulsion (evaporated and with more than 50% water content) is extremely difficult to ignite and to obtain self-sustained burning with. An unstable (i.e. our case) or a meso-stable emulsion can be ignitable. For the burning experiments, it was important to have a burning emulsion.

The physical properties of the crude oils and the corresponding artificial water-in-oil emulsions are shown in Table 1. The density and viscosity are averaged values measured at 25 °C obtained from various measurements conducted in a Paar Stabinger Viscometer SVM 3000. The viscometer follows various standards for measuring kinetic viscosities (ASTM D7042, EN16896, and DIN 51659-2), the dynamic viscosity (ASTM D7042), and the density (EN ISO 12185, ASTM D4052, and IP 365).

The herding agent OP40 is a proprietary polydimethylsiloxane copolymer and has a composition of more than 80% of 3-(Polyoxyethylene)propylheptamethyltrisiloxane according to the Material Safety Data Sheet (MSDS). This silicone copolymer has high thermal stability and is commonly used in daily-life applications; such as in household and automotive cleaning products, in hair conditioners, in skincare products, and in conventional agrichemicals. Furthermore, the silicone copolymer behaves like a liquid at room temperature, and it is described as a non-ionic amphiphilic copolymer [46]. The remaining <20% compounds of OP40 are unknown.

The herding agent ThickSlick6535 is composed of 65% of Sorbitan Monolaurate and 35% 2-ethyl-1-butanol according to the MSDS. The latter is an organic chemical compound slightly soluble in water and presents liquid behaviour at room temperature. The surfactant Sorbitan monolaurate is a combination of esters formed from the fatty lauric acid and polyols derived from sorbitol. This compound is used as a food additive (E number E493), in household cleaners, in cosmetics, creams, ointments, fragrances and toiletries [31]. The physical properties of the two herding agents are provided in Table 1.

Table 1 – Physical properties of the two crude oils, their corresponding 25% water-in-oil emulsions and of the herding agents.

<i>Properties</i>	<i>Crude oil¹</i>		<i>25 % water-in-oil emulsion</i>		<i>Herder²</i>	
	ANS	Grane	ANS	Grane	OP40	TS6535
Density at 25 °C [g/cm ³]	0.871	0.918	0.894	0.945	0.989	0.830
Kinematic viscosity [mm ² /s]	12.3	143.2	19.3	208.4		
Dynamic viscosity [mPa.s]	10.7	131.4	17.4	195.7	10-40	7.6
Flash point [°C]	-4	<23			>100	57
Pour point [°C]	13.9	1.3			23.4	-6

¹ The crude oil's flashpoint temperatures were obtained from the technical specifications.

² The properties of the herding agents were obtained from technical specifications and from Buist et al. [31] and from [47,48] .

2.2 Experimental matrix

The experimental matrix was designed to evaluate the thickening effect of the herding agents before and after ignition and burning of the crude oil. The experimental matrix can be seen in Figure 2. Most of the experiments were carried out without subsequent ignition. These experiments were classified according to the duration of the herding procedure: Short-duration experiments (0.5 hours), medium-duration experiments (up to 20 hours) and long-duration experiments (400 hours).

The short-duration experiments were further classified regarding the application order of the herder with respect to the oil. The *post-spill* application scenario refers to experiments where the herding agent was applied to the water basin after an oil slick was already established in equilibrium. This scenario corresponds to the real oil spill events where the herders would be used to thicken the spilled crude oil. For this scenario, the water temperature used was close to 0°C, the salinity was 32‰, and both crude oils (ANS and Grane), their respective artificial emulsion and both herders (OP40 and TS6535) were tested in triplicates (Figure 2, red arrows).

The *pre-spill* application scenario implies that the water basin was treated with the herding agents before the oil was added. As explained in the introduction, pre-spill application of herders is relevant for post-spill shoreline response or protection of important areas. Within this pre-spill herding scenario, the water had a temperature between 5 and 10 °C and tap water was used. Both herders were investigated with ANS and Grane crude oils and their corresponding artificial emulsions, as indicated by the blue arrows in Figure 2. No repetitions were carried out for the pre-applied scenarios.

Within the medium-duration (20 hours) and long-duration (400 hours) experiments only the post-spill application scenario was explored. In both duration scenarios, the non-saline water had initial temperatures in the range of 5 to 10 °C. In the long-duration experiments, the water temperature progressively increased to reach room temperatures (around 18 °C). For the medium-duration experiments, the thickening effectiveness of OP40 and TS6535 herders was studied on both crude oils and their respective artificial emulsions, as indicated by the yellow arrows in Figure 2. In the case of the long-duration experiments, only the fresh crude oils were tested with OP40 and TS6535 (black arrows in Figure 2). No repetitions were performed for either of the medium-duration or the long-duration experiments.

Only in the short-duration post-spill experiments, the crude oils were ignited and let to burn (indicated by the dashed arrows in Figure 2). For these experiments, only the fresh crude oils and the two herders were included. The herding effectiveness was analysed during the burning and after burn out; generally, 200 seconds after the flames died out.

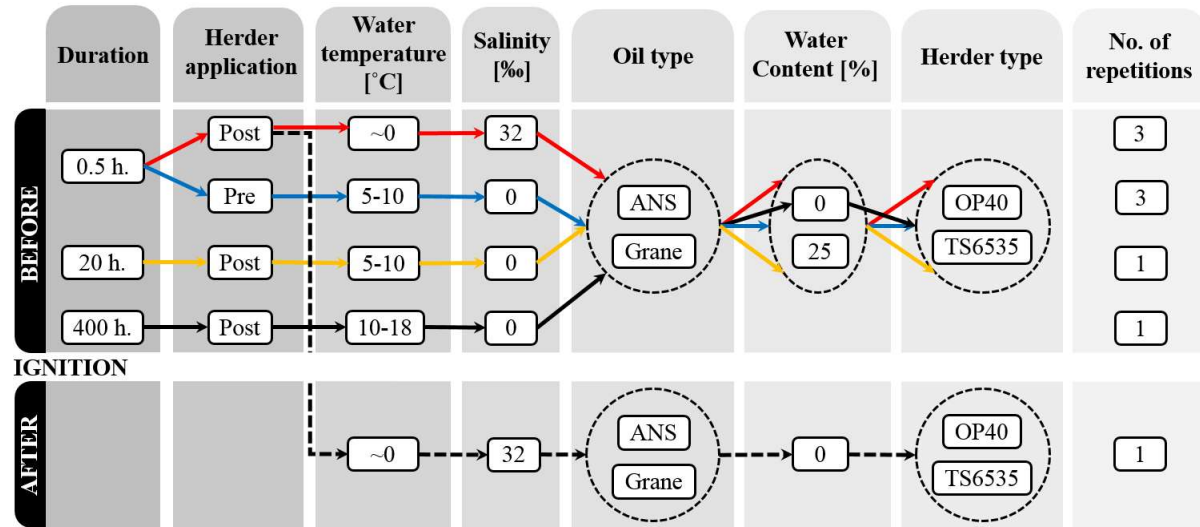


Figure 2 – The experimental matrix showing the various scenarios of the current study.

The experiments were conducted in a laboratory set-up called Crude Oil Flammability Apparatus (COFA). This small-scale apparatus has been successfully used in previous investigations to study the burning behaviour of crude oils for ISB [42,49,50], and the effectiveness of chemical herders [51]. The advantage of the COFA apparatus with respect to other experimental apparatuses used for ISB is that it can hold larger amounts of water; thus it can reproduce larger water-to-oil ratios closer to the real scenarios [49]. The COFA measures 1 m x 1 m x 0.5 m and contained approximately 390 litres of water for the current study, see Figure 3. For the experiments with fresh ANS and Grane crude oils, 200 ml of the oils were used respectively. For the emulsions, 300 ml were used in the experiments. A camera was located in a box above the experimental apparatus, see Figure 3. The box had fire-resistant glass in all its faces; this solution was deemed necessary since the oil slick burning had to be recorded to measure the slick area evolution.

Also, a Pyrex glass cylinder (PGC) was centrally located in the water basin. This arrangement had two aims. Firstly, the PGC's was needed to confine the oil slick partially and at the same time allow the movement of the oil slick during burning. Secondly, the cylinder enabled sampling of water for further analysis of the herder residues for other studies with results reported elsewhere [31,39]. Without any partial confinement, the herded oil slick drifts towards the basin walls during burning. As a consequence, re-radiation (during burning) from the basin's steel walls would have influenced the burning process. The oil slick was required to be centrally located during the burning experiments. Therefore, a 1-2 mm gap was created between the glass cylinder and the surface allowing the oil slick to be partially attached. The cylinder did not interfere with the herding procedure during the short-duration experiments. The Pyrex glass cylinder was only use in the short-duration experiments where burning was the target. After the herding procedure was completed, the water level in the COFA was slightly decreased through a drain in the bottom corner. The water was reduced until the distance from the water level to the upper edge of the cylinder was between 1 mm and 2 mm. See also Detail B in Figure 3.

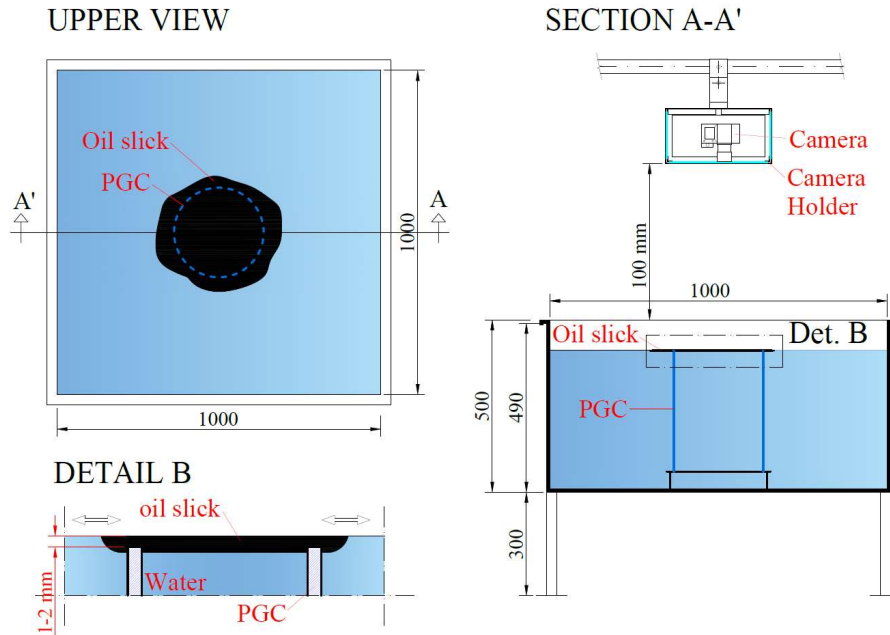


Figure 3 – Overview of the COFA apparatus. PGC refers to the Pyrex Glass Cylinder. The dimensions are in millimetres.

In all the post-spill experiments, the fresh or artificially emulsified crude oils were carefully added onto the water surface and were allowed to spread for 15-20 minutes until an equilibrium was reached. Then, the herder was added to the water basin at a dosage of $150 \mu\text{l}/(\text{m}^2 \text{ water surface})$, which is the recommended amount [31]. The herder was applied discretely from an electronic micropipette in the four corners of the water basin. For all the pre-spill applications, the recommended dosage of herder was applied on the water surface. Then, either the fresh or emulsified crude oil was carefully poured onto the centre of the already treated water surface.

Between each experiment, the COFA was thoroughly cleaned with a hot water solution of Alconox detergent (10 g/L) in order to remove possible herder residues. In addition, surface water samples were taken to measure the surface tension in a Wilhelmy plate to ascertain no herder residues remained from previous tests. If the water surface tension yielded values below 65 mN/m , the water was discarded, and the COFA cleaned once more before being refilled with water. The Wilhelmy procedure tends to result in lower surface tension values compared to other techniques (DuNouy ring); hence, the Wilhelmy technique is more conservative and was deemed adequate.

2.3 Data processing

The video recordings and pictures taken during the experiments were analysed in order to estimate the oil slick area and slick thickness. By knowing the initial poured mass of oil and its density, the oil thickness can be estimated. The area of the oil slick was estimated based on the number of black pixels in certain time-step frames. The recorded videos were processed by a script in MatLab which converted the time-step frames into a binary code, in other words, the script is capable of discriminating the black pixels (that correspond to the oil) from the rest of pixels. Subsequently, the total amount of black pixels (oil slick) was given by the program together with an illustration of the slick per interval frame. The illustration was compared to the corresponding time-step frame from the video, thereby ensuring uniformity and thorough results, see Figure 4.

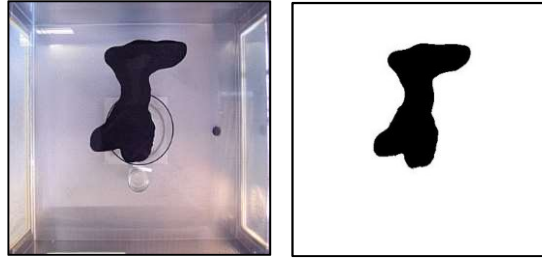


Figure 4 – Two-step analysis process of the videos: A frame was firstly selected from the video (left), and the area (in pixels) was given by the MatLab script, see the black pixel illustration (right).

Once the amount of black pixels representing the area of the oil slick is known, the area of the slick can be calculated in cm^2 . In order to do so a relationship was established between the size of several pixels and their equivalence in a certain length in cm. A picture was taken of a ruler placed at the water surface. After processing the picture, the equivalence of area in cm^2 to pixels can be found, and then the relationship can be calculated by using the following equation:

$$A_{\text{scale}} = \frac{A_{\text{cm}}}{A_{\text{px}}} (\text{cm}^2/\text{px}) \quad (1)$$

Where A_{cm} is the area in cm and A_{px} is the area in px. Once the relationship is calculated, it is multiplied by the area of the oil slick in pixels to convert the slick area into cm^2 . Finally, the oil slick thicknesses can be estimated by applying the following equation:

$$e_s = \frac{m_{0,\text{oil}}}{A_s \rho_{0,\text{oil}}} \quad (2)$$

Where m_{oil} is the mass of the poured oil/emulsion onto the water surface in g, A_s is the area of the slick in cm^2 and $\rho_{0,\text{oil}}$ is the density of the initial oil/emulsion in g/cm^3 .

This technique to estimate the oil slick area or flame area could not be applied during combustion of the crude oil because the flame changed the light conditions in the camera of each test. From the videos, several pictures were taken during the burning process and were subsequently manually analysed in AutoCAD software where the slick area could be estimated. The procedure in the CAD software had the same principles as in the previous procedure in MatLab. The mass of the left residue was weighed, and the density of the residues was measured in the Paar Stabinger Viscometer. Thus, after burning, the oil slick thickness could be estimated by using Equation (2).

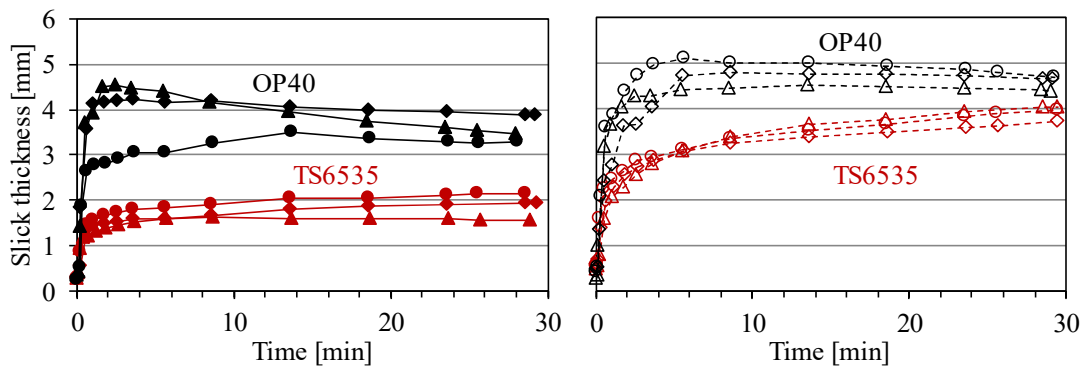
3. RESULTS AND DISCUSSION

The thickening effectiveness results are grouped into various sections following the scenarios in the experimental matrix. In the subsequent sections, 3.1 and 3.2, the oil slick thickness results from the short-duration (0.5 hours) experiments are presented for the post-spill and the pre-spill herder scenarios (with respect to the pouring of the oil), respectively. In Sections 3.3 and 3.4, the herding effectiveness results are presented for the medium-duration (20 hours) and for the long-duration (400 hours) experiments. Finally, the herding effectiveness results during and after combustion are presented in Section 3.5 based on the oil slick areas and flame area evolution.

3.1 Short-duration experiments with the post-spill herder procedure

The herding thickening effect of both herders, OP40 and TS6535, on ANS crude oil, can be seen in Figure 5. The oil slick thickness achieved by OP40 was approximately between 3 and 4 mm. TS6535, on the contrary, obtained lower oil slick thickness with the same crude oil. This herding agent thickened the oil at a much slower pace than OP40 within the first 100 seconds after being applied onto the water. Then, steady thickening was observed during the test period. Similarly, for the ANS emulsions (25% water content), the OP40 obtained greater oil slick thicknesses than those obtained by TS6535, see Figure 5. TS6335 demonstrated a different behaviour, non-steady during the execution of the test. As it can be seen in Figure 5, the emulsion slick thickness was progressively being thickened. These results show that it will take more than 30 minutes to reach a maximum slick emulsion thickness.

There are some similarities but also discrepancies when comparing the previous results to alike results found in the literature (APPENDIX B). The present TS6535 results for ANS are quantitatively and qualitatively similar to those conducted in a 1m2 rig reported by Potter, Buist and co-workers [30,31] (see Figure B. 3). However, other literature results are distinctively different [4,21,29] (see Figure B. 3). The present OP40 results on ANS diverge slightly from those in literature [29–31] in thickening behaviour (see Figure B. 2). Finally, on emulsified ANS, the present results with both herder also differ from literature results [31](see Figure B. 5).



Herder	Symbol	Trial	Water content [%]	T _{water} [°C]	Salinity [‰]	Herder	Symbol	Trial	Water content [%]	T _{water} [°C]	Salinity [‰]
OP40	▲	1	0	~0.0	32	TS6535	▲	1	0	~0.0	32
	◆	2		~0.0	32		◆	2		~0.0	32
	●	3		~0.0	32		●	3		~0.0	32
	-△--	1	25	~0.0	32		-△--	1	25	~0.0	32
	-◇--	2		~0.0	32		-◇--	2		~0.0	32
	-○--	3		~0.0	32		-○--	3		~0.0	32

Figure 5 – Average slick thickness as a function of time. Various replicate runs for fresh and weathered ANS crude thickened with the herders OP40 and TS6535.

A similar difference in thickening effectiveness was observed when Grane crude oil was herded by both herders. OP40 was again quicker in thickening in the beginning and achieved greater oil slick thickness than TS6535, see Figure 6. Furthermore, thicker oil slick thicknesses were achieved by OP40 with Grane than with ANS, while the contrary was found for TS6535. In two experiment runs Grane with TS6535, the slick thickness achieved was 1mm, which is the minimum thickness to attain ignition. When the emulsified Grane (with 25% water content) was herded with OP40, the oil slick thickened at a much slower pace in the beginning, and thinner oil slick thicknesses were achieved than in the experiments with fresh Grane, see Figure 6. TS6535 showed a slightly greater slick thickness with 25% water-in-oil Grane emulsion than in the case of fresh crude Grane.

For fresh Grane, the present results with OP40 are also qualitatively different from those reported by Buist and co-workers [31]. The most significant antagonistic differences are observed with respect to TS6535 on Grane, where this crude oil was effectively herded with thickness in excess of 4 mm [31,32].

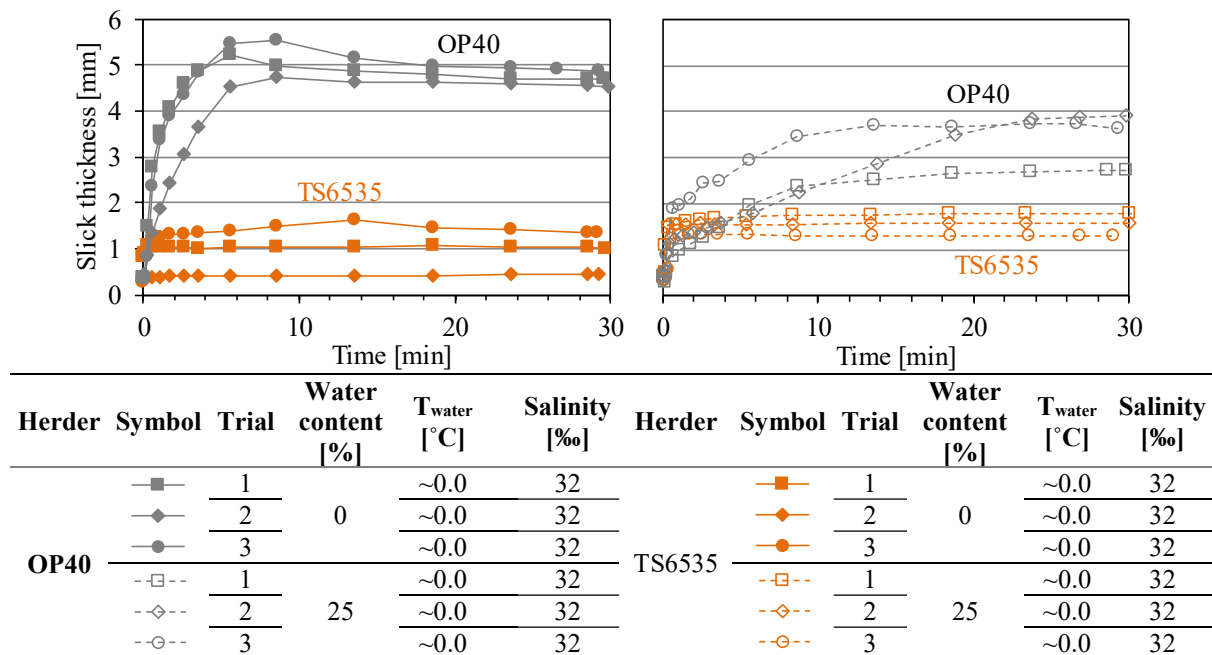


Figure 6 – Average slick thickness as a function of time. Various replicates run for fresh and weathered Grane crude thickened with the herders OP40 and TS6535.

The present results show that there were cases where both herders were more efficient for the emulsified oils than for the fresh oils. In all cases, OP40 was more efficient than TS6535. When comparing ANS against Grane, both herders turned out to be less effective for Grane (apart from fresh Grane with OP40), which is in contradiction to previous findings [33,34]. In short, the present results add more discrepancy to the results from the literature (see Section 1). It is difficult to elucidate the physical phenomena that could explain such discrepancies.

However, for some of the behaviour observed, there might be two potential explanations. Firstly, on the emulsified crude oils, the weathering methodology might by one the parameters that exert a great influence on the results. Secondly, the poor results obtained by TS6535 on Grane could be associated with the formation of sheens. During the execution of these experiments, sheens were formed around the slick prior to herding. Buist and co-workers

reported that TS6535 performed poorly on ANS sheen [4,21]. Similar behaviour was observed on another oil (Chayvo). However, Chayvo could be thickened by a shoreline agent [4,29].

Some authors have claimed that sheens might have a different spreading regime (spreading pressure) than the crude oil [52,53]. This hypothesis (not proven though) can be strengthened the fact that sheens undergo faster evaporative losses [54]; thereby their surface tension properties changes [27,28] (it could be very different from the oil).

3.2 Medium-duration experiments

The slick thickness results for experiments with 20 hours of herding for both fresh crude oils and their respective 25% water-in-oil emulsions can be seen in Figure 7. It has to be pointed out that the evaporative losses for Grane were assumed to be negligible since it will be less than approximately 10% [55]. It was estimated that due to evaporation Grane would have had an increase of 2% in density. Hence, little effect was expected on the estimation of the oil slick thickness which is based on the density of the crude oil. ANS is a medium-heavy crude oil, and it can be expected to suffer higher evaporative losses [30]. After 20 hours, the thickness of ANS, taking into account the evaporation, would be 27% lower than the originally estimated thickness shown in Figure 7. Such an evaporation rate would affect the slick thickness results quantitatively. However, after comparing the results with and without taking into account the evaporation rate, the main behaviour remained qualitatively the same.

The herding agent OP40 presented a distinctive behaviour in these longer duration experiments with respect to the short-duration tests, as it can be observed in Figure 7 (left pane). In general, the thickening effect of OP40 has two phases. The first is a peak-phase that lasted up to approximately one hour, and a maximum oil slick thickness was achieved for all the crude oils and emulsions. Second, the decay-phase where the oil slick thickness suffered a decay for over 6 hours. The full thickening effect (holding thick slick thicknesses) of the OP40 seems to last one hour, and the 30 min duration of the short-term test might not have been enough to observe the maximum peak behaviour in thickening effect.

The herding agent TS6535 presented, on the contrary, an opposite behaviour as it can be seen in Figure 7 (right pane). TS6535 thickened both crude oils and emulsions within the first minutes. Thereafter, a steady-state period followed during the duration of the test with no further increase in thickness or decay in thickening effect. The exception was the TS6535 used with emulsified ANS, where the steady-phase was achieved after 5 hours.

The contrast in decay behaviour between both herders on the crude oils might be associated with the dispersion of the herder (its components) in water. However, there is no data available for the rate of dispersion or for whether the herder would dissolve or not. The evaporation of the TS6535 herder is deemed negligible because the vapour pressure of its components is very low. In the case of OP40, there is no information available about its vapour pressure. In the field, other plausible degradation mechanisms are biodegradation and photo-degradation [36].

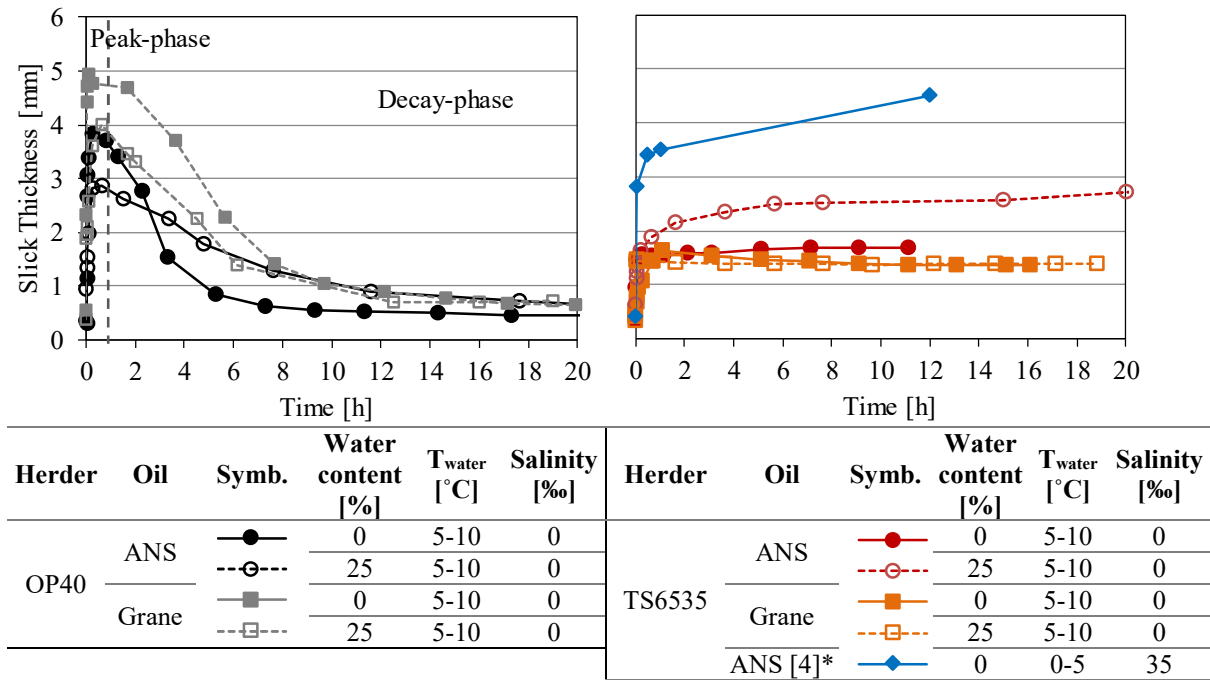


Figure 7 – Average slick thickness as a function of time. Results from the long-duration experiments for fresh and weathered ANS and Grane crude oils herded with OP40 (Left pane) and TS6535 (Right pane). In the right pane, results from another study [4] is also presented for comparison (* Presence of ice block was part of the current study). In some experiments, the recording did not last 20 hours due to power failure of the cameras.

The thickening effectiveness of both herding agents during the medium-duration experiments (comparing during the first 30 minutes) resulted in generally similar behaviour as those obtained in the short-duration tests in Figure 5 and Figure 6. The only exception was observed in emulsified ANS herded with OP40. In that medium-duration experiment, the thickening behaviour resulted poorer compared to the short-duration tests. Results found in the literature are also depicted in Figure 7 for comparison. The thickening effectiveness of TS6535 on ANS reported by Buist et al. [4] is better than the results obtained in this study with ANS.

These results show that the efficiency of these herders should not only be defined by the thickness achieved, but also by the capacity of both herders to last more extended periods. Hence, OP40 should be used for rapid operations, whereas TS6535 might be better suited for longer duration operations.

3.3 Short-duration experiments with the pre-spill herder procedure

The pre-spill test results for both herding agents on fresh ANS and Grane crude oils and their corresponding artificial emulsions (25 % water content) are displayed in Figure 8. As it can be seen, the oil was not allowed to spread initially, particularly for fresh ANS crude oil and emulsified ANS, and a subsequent slight decrease followed. Overall, it can be seen that both herders showed greater effectiveness on the fresh crude oils than on the corresponding emulsifications, the only exception was in the ANS crude oil with TS6535.

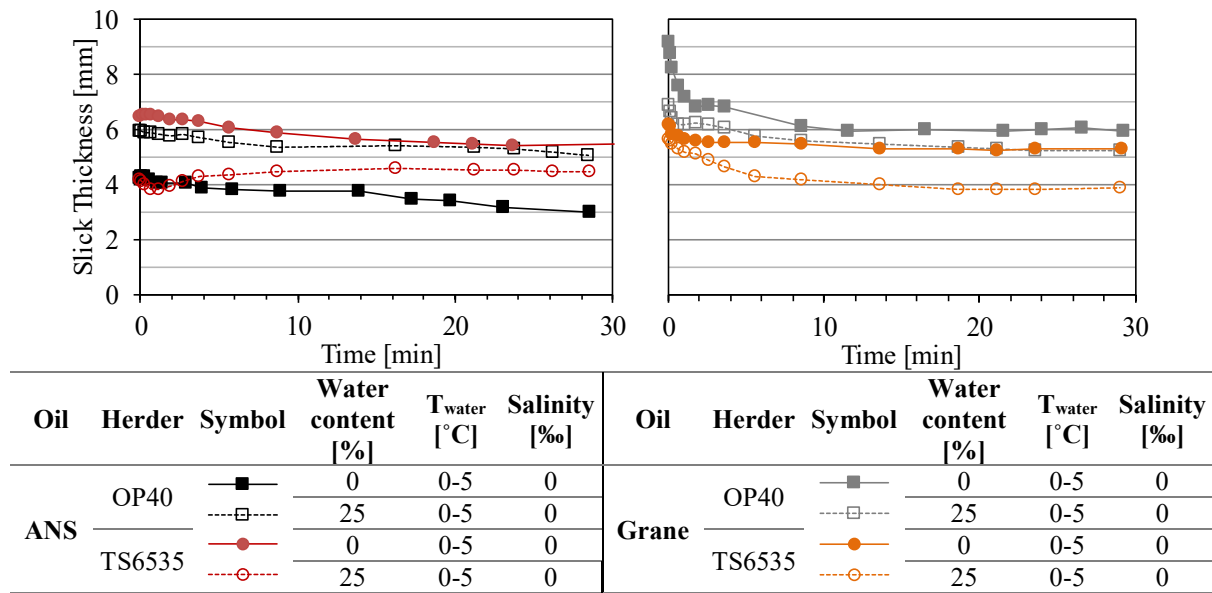


Figure 8 – Oil slick thickness as a function of time. Results from the pre-spill experiments for both fresh and weathered ANS and Grane crude oils herded with OP40 and TS6535.

Compared to post-spill test results in Section 3.1, the results obtained in the pre-spill tests generally achieved more efficient thicknesses. The exception was, however, with OP40 on fresh and emulsified ANS. Despite this discrepancy, the present results are in alignment with those from [4,33] where pre-spill was more efficient than post-spill. Anecdotally, the herder TS6535 was able to obtain thicker thickness in the pre-spill experiments than in the post-applied tests where TS6535 showed poor behaviour (thin thickness). Despite the small discrepancies, the results might be explained by the equilibrium thickness of the oil. This equilibrium thickness is defined as the transition from gravity-viscous regime to surface tension-viscous regime [4]. Each regime has its own spreading pressure, but it is not clear whether the spreading regime of the oil could affect the herding efficiency of the herders.

3.4 Long-duration experiments

Grane and ANS fresh crude oils were thickened with TS6535 for longer periods of time, up to 400 hours (16 days), and the oil slick thickness evolution during the test for both oils are displayed in Figure 9. Due to the long time under which both crude oils were in the laboratory conditions, the evaporative losses were taken into account when estimating the slick thickness. This correction of the oil slick thickness was especially significant in the case of ANS, which after 60 hours can lose up to 40% by volume [30].

As it can be seen in Figure 9, TS6535 achieved the greatest thickness on Grane crude oil, where an increasing period lasted 10 hours approximately, and a maximum oil slick thickness was achieved. On the contrary, the increase in thickness phase for ANS lasted much longer than for Grane. The maximum slick thickness achieved by ANS was reached after 80 hours. Grane crude oil suffered two decay phases after reaching a maximum slick thickness. The first phase was characterised by having a steady rate of $8.8 \cdot 10^{-3}$ mm/h. After 370 hours, Grane suffered a second decay phase with a faster rate of $21.8 \cdot 10^{-3}$ mm/h. These rates were lower than the decreasing rate experience by ANS crude oil in the decay phase, which was $77 \cdot 10^{-3}$ mm/h.

This difference in declining behaviour might be potentially explained by the difference in oil properties [30,55]. Both crude oils experience different evaporative losses, where ANS presents much higher evaporative losses than Grane. As the weathering degree increases, so does the surface tension of the crude oil [27,28]. In turn, the surface tension of both crude oil

might have changed at different paces. Furthermore, another plausible explanation is the dissolution and dispersion of the monolayer created by the herder at the edges of the oil slick, which might also happen at different rates depending on each crude oil. There is no information in the literature because limited or no research has been conducted on the subject. As such, the statement is merely a hypothesis and only further experiments will elucidate the nature of this behaviour in slick thickness.

The oil slick thickness results achieved in this long-duration tests differ from those obtained earlier, as seen in Figure 7, as the long-duration experiments resulted in more efficient thickening behaviour than in the medium-duration experiments. The test conditions were almost identical, though with two minor differences. The first difference was the water temperature, as the long-duration tests were conducted during spring and the tap water temperature was 5-10 °C higher than for the medium-duration tests. The second difference is that in the long-duration experiments, the oil drifted towards the basin edge (according to the recording).

From an oil spill perspective, TS6535 might be the best choice to contain spilt oil during large periods of time in a closed environment such as a lake. To the knowledge of the authors, there are no experimental studies that have looked at the thickening capabilities of both herding agents for such a long period of time. Therefore, more studies should be carried out in the future.

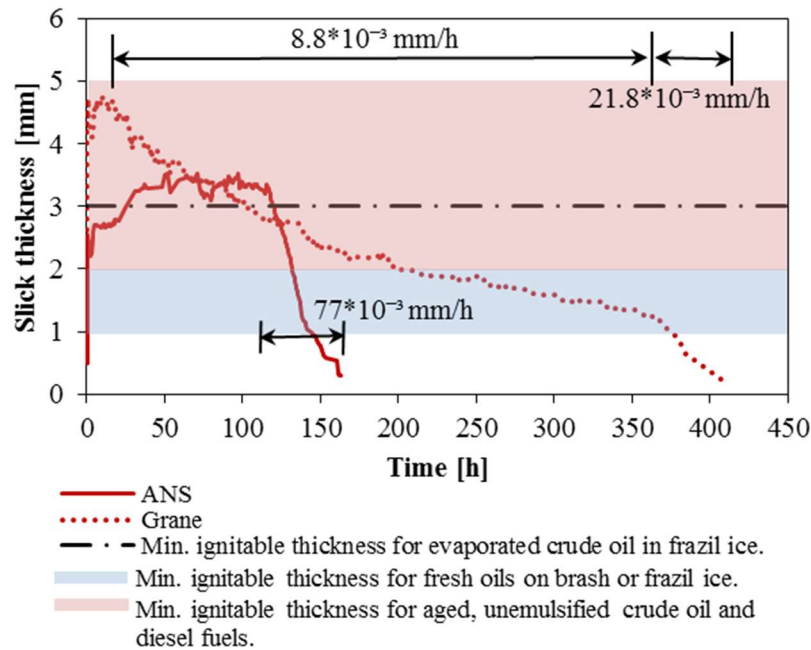


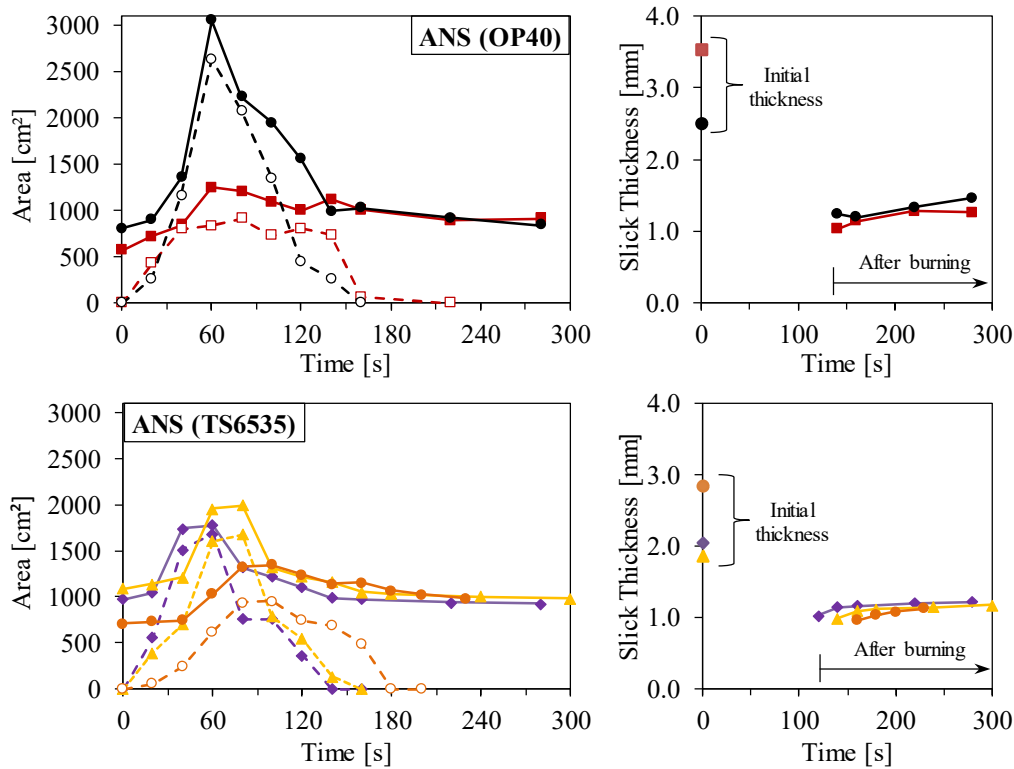
Figure 9 – Average slick thickness as a function of time. Corrected results from long-duration experiments with both fresh crude oils herded with TS6535 and minimum ignitable thickness for crude oil under several scenarios [1,2,15]. The water temperature ranged from 10 to 18 °C, and the salinity was 0‰.

3.5 Herding effectiveness during and after burning

The herding effectiveness regarding oil slick area during and after combustion for various replicate tests of fresh ANS and Grane crude oils are displayed in Figure 10 and Figure 11, respectively (actual images are shown in APPENDIX C). In the same illustrations, for each

replicate test, the corresponding flame area covering the oil slick area and the oil slick thickness (after flames died out) is displayed. Consistently, in all tests, the oil slick expanded during combustion due to most likely heat transfer changing the surface and interfacial tension between the oil slick, the water and the monomolecular surface layer created by the herding agent. Once the flames started to retract, both herding agents seemed to be able to re-thicken the oil slick as this cooled down. After the flames died out, the oil slick was further thickened with certain differences for each oil. In the case of ANS, the oil slick was mildly thickened by both herders as seen in the right panes in Figure 10. On the contrary, both herders were able to thicken significantly Grane crude oil once the burning finished, see the right panes in Figure 11.

It is clear that the monomolecular layer has lower thickening capabilities on the hot oil slick (since it possibly has stronger surface tension properties). At this test scale, these results indicate that the monomolecular created by the herder layer does not suffer a substantial deterioration in thickening effectiveness during burning (due to radiation). However, in a large-scale experiment or the field, the radiation from the burning oil slick might be much larger and could potentially affect the monomolecular layer. In the future, new technologies, such as acoustic sensors in the water column, could potentially be used to evaluate the oil slick thickness during and after burning as it was demonstrated in a recent work conducted by Panetta and co-workers [56].













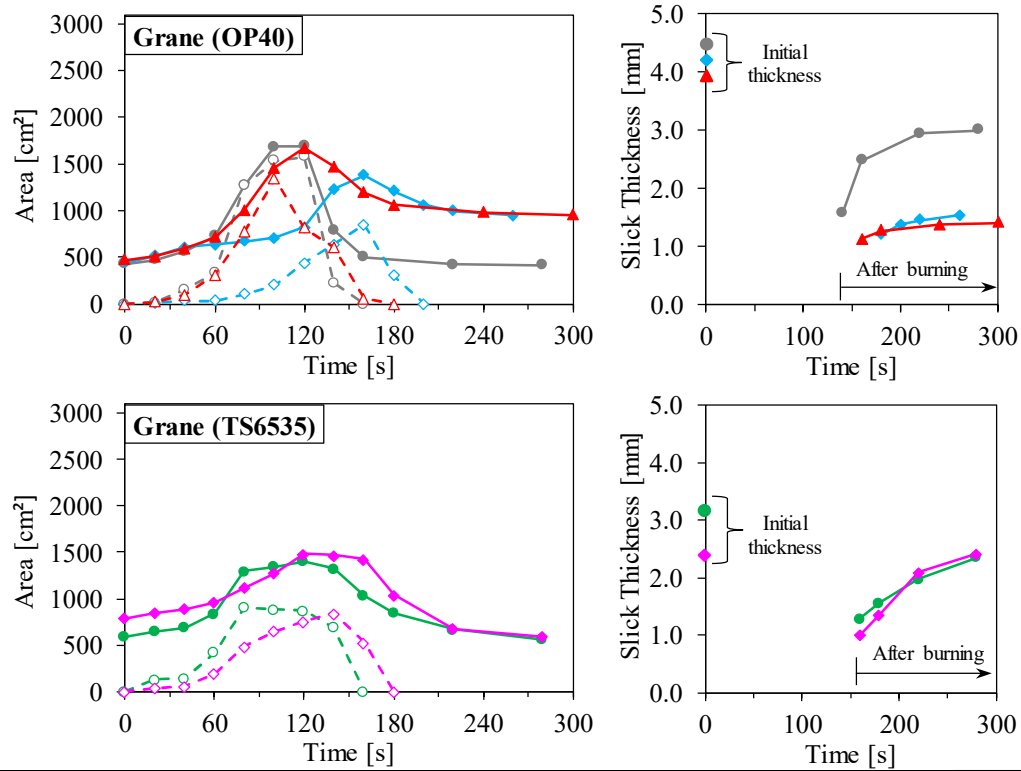
Herder	Symb.	Component	Trial	T _{water} [°C]	Herder	Symb.	Component	Trial	T _{water} [°C]			
OP40		Oil slick	1	~0.0	TS6535		Oil slick	1	~0.0			
		Flames					Flames					
		Oil slick	2				Oil slick	2				
		Flames					Flames					
							Oil slick	3				
							Flames					

Figure 10 – Oil slick area (black lines) and the corresponding flame area (dash lines) during and after burning for various replicates of ANS oil herded with OP40 and TS6535. The oil slick thickness after burning are also represented in the right panes for each test.













Herder	Symb.	Component	Trial	T _{water} [°C]	Herder	Symb.	Component	Trial	T _{water} [°C]
OP40		Oil slick	1	~0.0	TS6535		Oil slick	1	~0.0
		Flames					Flames		
		Oil slick	2	~0.0			Oil slick	2	~0.0
		Flames					Flames		
		Oil slick	3	~0.0					
		Flames							

Figure 11 – Oil slick area (black lines) and the corresponding flame area (dash lines) during and after burning for various replicates of Grane oil herded with OP40 and TS6535. The oil slick thickness after burning are also represented in the right panes for each test.

4. CONCLUSIONS

The herding experiments presented herein were conducted in a 1m² basin (closed cell) and in calm conditions. Thereby, the results presented herein should be taken as illustrative, and large-scale experiments in real scenarios are encouraged. The experimental study along with the comparative analysis of the literature review resulted in the following findings.

Both herding agents, i.e. the hydrocarbon-based (TS6535) and the silicone-based (OP40) exhibited good thickening effectiveness for the experimental conditions studied, and they routinely achieved slick thicknesses in excess of 1 mm. The present results show that OP40 is the most efficient (greater thickness) for short periods, whereas TS6535 can hold its thickening capabilities for extended periods (up to 350 hours). The pre-spill application was found to be more efficient than post-spill application. During ISB, the thickening capabilities of the herders are compromised. However, after burning, the surface monolayer created by the herder was still active and did not deteriorate due to radiative heat feedback from the flames.

Results across different studies, including this, showed contradictions and inconsistencies in thickening behaviour for OP40 and TS6535 on both crude oils over a range of parameters. For instance, the poor performance of TS6535 on Grane might be associated with the sheen formation (although it remains unclear). It is then challenging to establish confidently the physical dependencies of both herders' behaviour on the parameters studied. The literature data should be critically regarded as there are still many inconsistencies and knowledge gaps.

Future studies should attempt to elucidate the effect of important parameters on the herder's efficiency by looking into an in-depth physical/chemical analysis (viscosity, SARA content, and others). Also, better and reliable experimental procedures should be developed to clarify and determine the inconsistency in the results for both herders. Among the aspects that require further attention are: pre-spill application of herder for oil spill response (shoreline scenarios, in protected areas and lakes), formation and role of sheens on herding as this problem might affect the method negatively, the herder effect for emulsified oils, the mechanisms behind the decay of the herding agents and their fate once the ISB has finished. Further research on chemical and environmental aspects are needed to understand these mechanisms.

Acknowledgements

This paper was prepared under contract for the International Association of Oil & Gas Producers (IOGP) by S.L. Ross Environmental Research Ltd as prime contractor. Publication of this paper does not necessarily imply that the contents reflect the views and policies of IOGP, nor are there any implied IOGP endorsements of studies performed and results presented by SL Ross or by the subcontracting partners DCE and DTU. The authors would like to thank Bjørn Skjønning Andersen for his assistance during the experimental part of the work.

REFERENCES

- [1] I.A. Buist, S.G. Potter, B.K. Trudel, S.R. Shelnutt, A.H. Walker, D.K. Scholz, P.J. Brandvik, J. Fritt-Rasmussen, A.A. Allen, P. Smith, In Situ Burning in Ice-affected waters: State of Knowledge report, 2013.
<http://www.arcticresponsetechnology.org/research-project/in-situ-burning-of-oil-in-ice-affected-waters-state-of-knowledge/>.
- [2] S. Potter, I. Buist, In-Situ Burning for Oil Spills in Arctic Waters : State-of-the-Art and Future Research Needs, in: W.F. Davison, K. Lee, A. Cogswell (Eds.), *Oil Spill Response A Glob. Perspect.*, NATO Scien, Springer Dordrecht, 2008: pp. 23–39.
doi:10.1007/978-1-4020-8565-9_5.
- [3] J. Fritt-Rasmussen, P.J. Brandvik, Measuring ignitability for in situ burning of oil spills weathered under Arctic conditions: From laboratory studies to large-scale field experiments, *Mar. Pollut. Bull.* 62 (2011) 1780–1785.
doi:10.1016/j.marpolbul.2011.05.020.
- [4] I. Buist, S. Potter, T. Nedwed, J. Mullin, Herding surfactants to contract and thicken oil spills in pack ice for in situ burning, *Cold Reg. Sci. Technol.* 67 (2011) 3–23.
doi:10.1016/j.coldregions.2011.02.004.
- [5] A.A. Allen, Contained controlled burning of spilled oil during the Exxon Valdez oil spill, *Spill Technol. Newsl.* 15 (1990) 1–5.
- [6] C.C. Guénette, P. Sveum, C.M. Bech, I.A. Buist, Studies of in situ burning of emulsions in norway, in: *Int. Oil Spill Conf.*, American Petroleum Insitute, Long Beach, California (US), 1995: pp. 115–122.
- [7] P.J. Brandvik, J. Fritt-Rasmussen, R. Daniloff, F. Leirvik, Using a Small Scale Laboratory Burning Cell to Measure Ignitability for In Situ Burning of Oil Spills as a Function of Weathering, in: *Thirty-Third AMOP Tech. Semin. Environ. Contam. Response*, Environment Canada, Halifax, Nova Scotia, Canada, 2010: pp. 755–771.
- [8] P.J. Brandvik, P.D. Snorre, L.-G. Faksness, J. Fritt-Rasmussen, R. Lundmark Daae, F. Leirvik, Report no. 26: Experimental oil release in broken ice. A large-scale field verification of results from laboratory studies of oil weathering and ignitability of weathered oil spills., 2010.
- [9] D. Evans, W.D. Walton, H.R. Baum, K.A. Notarianni, J.R. Lawson, H.C. Tang, K.R. Keydel, R.G. Rehm, D. Madrzykowski, R.H. Zile, In-situ Burning of Oil Spills: Mesoscale Experiments, in: *Fifteenth Arct. Mar. Oil Spill Progr. Tech. Semin.*, Environment Canada, Edmonton, Canada, 1992: pp. 593–657.
<http://www.fire.nist.gov/bfrlpubs/fire03/PDF/f03159.pdf>.
- [10] R.J. Bullock, S. Aggarwal, R.A. Perkins, W. Schnabel, Scale-up considerations for surface collecting agent assisted in-situ burn crude oil spill response experiments in the Arctic: Laboratory to field-scale investigations, *J. Environ. Manage.* 190 (2017) 266–273. doi:10.1016/j.jenvman.2016.12.044.
- [11] R. Wighus, L.E. Lønvik, Fire on the sea surface - Experiments at Svalbard 1994. Summary report of the winter and summer experiments, Trondheim - Norway, 2007.
<https://rise.fr.no/media/publikasjoner/upload/nbl-a07132.pdf>.
- [12] O.B.C.S. and E.T. The Federal Interagency Solutions Group, *Oil Budget Calculator: Deepwater Horizon*, National Incident Command, Washington, D.C., 2010.
- [13] A.A. Allen, D. Jaeger, N.J. Mabile, D. Constanzo, The Use of Controlled Burning during the Gulf of Mexico Deepwater Horizon MC-252 Oil Spill Response, in: *Int. Oil Spill Conf.*, 2011: p. 194. <https://doi.org/10.7901/2169-3358-2011-1-194>.
- [14] S. Aggarwal, W. Schnabel, I. Buist, J. Garron, R. Bullock, R. Perkins, S. Potter, D. Cooper, Aerial application of herding agents to advance in-situ burning for oil spill

- response in the Arctic: A pilot study, *Cold Reg. Sci. Technol.* 135 (2017) 97–104. <http://dx.doi.org/10.1016/j.coldregions.2016.12.010>.
- [15] J. Fritt-Rasmussen, In situ burning of Arctic marine oil spills - Ignitability of various oil types weathered at different ice conditions. A combined laboratory and field study (PhD Dissertation), Technical University of Denmark, 2010. http://orbit.dtu.dk/files/5186132/All_Final_JFR.pdf.
 - [16] A.B. Nordvik, M.A. Champ, K.R. Bitting, Estimating Time Windows for Burning Oil at Sea: Processes and Factors, *Spill Sci. Technol. Bull.* 8 (2003) 347–359. doi:10.1016/S1353-2561(03)00097-5.
 - [17] J.L. Torero, S.M. Olenick, J.P. Garo, J.P. Vantelon, Determination of the burning characteristics of a slick of oil on water, *Spill Sci. Technol. Bull.* 8 (2003) 379–390. doi:10.1016/S1353-2561(03)00071-9.
 - [18] N. Wu, G. Kolb, J.L. Torero, The Effect of Weathering on the Flammability of a Slick of Crude Oil on a Water Bed, *Combust. Sci. Technol.* (2007) 37–41.
 - [19] I. Buist, S. Potter, Barents Sea Field Test of Herder to Thicken Oil for In situ Burning in Drift Ice, in: *Proc. Thirty-Third AMOP Tech. Semin. Environ. Contam. Response*, Environment Canada, Ottawa, Ontario, 2010: pp. 725–742.
 - [20] I. Buist, S. Potter, T. Nedwed, J. Mullin, Field research on using oil herding surfactants to thicken oil slicks in pack ice for in situ burning, in: *Arct. Mar. Oilspill Progr. Tech. Semin.*, Environment Canada, Edmonton, Canada, 2007: p. 403.
 - [21] I. Buist, S. Potter, T. Nedwed, J. Mullin, Herding Agents Thicken Oil Spills in Drift Ice to Facilitate In Situ Burning: A new Trick for an Old Dog, in: *Int. Oil Spill Conf.*, American Petroleum Institute, 2008: pp. 673–679. <https://doi.org/10.7901/2169-3358-2008-1-i>.
 - [22] T. Nedwed, A. Tidwell, I. Buist, R. Belore, G. Canevari, Advances in treating agents for oil spill reponse, in: *SPE/APPEA Int. Conf. Heal. Safety, Environ. Oil Gas Explor. Prod.*, Society of Petroleum Engineers, Perth, Australia, 2012.
 - [23] P. Lane, P. Newsom, I. Buist, T. Nedwed, A. Tidwell, K. Flagg, Recent efforts to develop and commercialize oil herders, in: *35th AMOP Tech. Semin. Environ. Contam. Response*, Vancouver, BC, Canada, 2012: pp. 472–479.
 - [24] P.J. Brandvik, J. Lise, M. Resby, P. Snorre, F. Leirvik, J. Fritt-Rasmussen, Report no. 19: Meso-Scale weathering of oil as a Function of Ice conditions. Oil properties, dispersibility and In Situ Burnability of Weathered Oil as a Function of Time., 2010.
 - [25] P.S. Daling, M.Ø. Moldestad, Ø. Johansen, A. Lewis, J. Rødal, Norwegian Testing of Emulsion Properties at Sea—The Importance of Oil Type and Release Conditions, *Spill Sci. Technol. Bull.* 8 (2003) 123–136. doi:10.1016/S1353-2561(03)00016-1.
 - [26] D.D. Evans, W.D. Walton, H.R. Baum, K.A. Notarianni, E.J. Tennyson, Mesoscale Experiments Help to Evaluate In-situ Burning of Oil Spills, in: *Internaitonal Oil Spill Conf.*, API Publishing Services, 1220 L Streetm N.W., Washington, D.C. 20005, Tampa, Florida, 1993: pp. 755–760.
 - [27] B. Hollebone, Measurement of Oil Physical Properties, *Oil Spill Sci. Technol.* (2011) 63–86. doi:10.1016/B978-1-85617-943-0.10004-8.
 - [28] A. V. Soloviev, B.K. Haus, M.G. McGauley, C.W. Dean, D.G. Ortiz-Suslow, N.J.M. Laxague, T.M. Özgökmen, Surface dynamics of crude and weathered oil in the presence of dispersants: Laboratory experiment and numerical simulation, *J. Geophys. Res. Ocean.* 121 (2016) 3502–3516. doi:10.1002/2015JC011533.
 - [29] I. Buist, G. Canevari, T. Nedwed, New Herding Agents for Thickening Oil Slicks in Drift Ice for In Situ Burning, in: *Proc. 33th AMOP Tech. Semin. Environ. Contam. Response*, Environment Canada, Halifax, Nova Scotia, Canada, 2009.
 - [30] S. Potter, I. Buist, D. Cooper, W. Schnabel, J. Garron, R. Perkins, S. Aggarwal, R.

- Bullock, P. Lane, Field Research on Helicopter Application of Chemical Herders to Advance In-Situ Burning, 2016. <http://www.arcticresponsetechnology.org/>.
- [31] I. Buist, D. Cooper, K. Trudel, J. Fritt-Rasmussen, S. Wegeberg, K. Gustavson, P. Lassen, W.U. Rojas Alva, L. Zabilansky, Research investigations into herder fate, effects and windows-of-opportunity, 2017. http://www.arcticresponsetechnology.org/wp-content/uploads/2017/09/research-investigations-into-herder-fate_-effects-and-windows-of-opportunity-final-february-1-2017.pdf.
- [32] I. Singsaas, D. Cooper, I. Buist, S. Potter, A. Lewis, P.S. Daling, M. Bråtveit, Field experiment to validate herder and in-situ burning in open water, 2017. <http://arcticresponse.wpengine.com/wp-content/uploads/2017/11/Report-Field-Experiment-to-Valid.pdf>.
- [33] U. Rojas-Alva, B. Skjønning Andersen, G. Jomaas, Chemical herding of weathered crude oils for in-situ burning, *J. Environ. Manage.* 250 (2019) 109470. doi:<https://doi.org/10.1016/j.jenvman.2019.109470>.
- [34] Z.A. Kulekeyev, G.K. Nurtayeva, E.S. Mustafin, A.A. Ainabayev, T.E. Mustafin, A.S. Borsynbayev, G.A. Zharikessov, Using herders for oil spill response in the sea, *Natl. Acad. Sci. Repub. Kazakhstan*. 5 (2018) 58–66. doi:doi.org/10.32014/2018.2518-1491.8.
- [35] P.D. Byrne, Richard, H. Du Panetta, P. Alexandria, Determining the Operability Limits of Chemical Herders, Sterling, VA, 2018. <https://www.bsee.gov/sites/bsee.gov/files/research-reports//1075aa.pdf> (accessed October 10, 2019).
- [36] R.J. Bullock, R.A. Perkins, S. Aggarwal, In-situ burning with chemical herders for Arctic oil spill response: Meta-analysis and review, *Sci. Total Environ.* 675 (2019) 705–716. doi:[10.1016/J.SCITOTENV.2019.04.127](https://doi.org/10.1016/J.SCITOTENV.2019.04.127).
- [37] I. Buist, Mid-scale test tank research on using oil herding surfactants to thicken oil slicks in pack ice: An update, in: *Environ. Canada Arct. Mar. Oil Spill Progr. Tech. Semin. Proc.*, Environment Canada, Vancouver, BC, Canada, 2006: pp. 691–709.
- [38] D. Cooper, I. Buist, S. Potter, P. Daling, I. Singsaas, A. Lewis, Experiments at Sea with Herders and In Situ Burning (HISB), in: *Int. Oil Spill Conf., IOSC, Long Beach, CA, USA, 2017*: pp. 2184–2203. doi:<https://doi.org/10.7901/2169-3358-2017.1.2184>.
- [39] U. Rojas-Alva, J. Fritt-Rasmussen, G. Jomaas, Small-scale in-situ burning (ISB) experiments with chemically confined crude oils on water (accepted), *Fire Saf. J.* (2019).
- [40] J. Fritt-rasmussen, K. Gustavson, S. Wegeberg, E.F. Møller, D. Nørregaard, P. Lassen, I. Buist, D. Cooper, K. Trudel, U. Rojas Alva, G. Jomaas, Ongoing Research on Herding Agents for In Situ Burning in Arctic Waters: Studies on Fate and Effects, in: *Int. Oil Spill Conf., Long Beach, California (US), 2017*: pp. 2976–2995. <https://doi.org/10.7901/IOSC-2017-1-fm.1>.
- [41] D. Mackay, W. Zagorski, Studies of water-in-oil emulsions, Environment Canada. Environmental Protection Service. Environmental Impact Control Directorate. Environmental Emergency Branch. Research And Development Division, Ottawa, Ontario, 1982.
- [42] U. Rojas Alva, B. Skjønning Andersen, G. Jomaas, Pumice stones as potential in-situ burning enhancer, *Cold Reg. Sci. Technol.* 146 (2018) 167–174. doi:[10.1016/j.coldregions.2017.12.004](https://doi.org/10.1016/j.coldregions.2017.12.004).
- [43] M. Fingas, B. Fieldhouse, J. Mullin, Studies of water-in-oil emulsions and techniques to measure emulsion treating agents, in: *Arct. Mar. Oil Spill Progr. Tech. Semin.*, Ministry of Supply and Services, Canada, 1994: pp. 213–242.

- <https://www.bsee.gov/sites/bsee.gov/files/osrr-oil-spill-response-research/120bi.pdf>.
- [44] M. Fingas, B. Fieldhouse, *Water-in-oil Emulsions: Formation and Prediction*, First, John Wiley & Sons, 2015. doi:10.1002/9781118989982.
 - [45] J.P. Garo, J.P. Vantelon, J.M. Souil, C. Breillat, Burning of weathering and emulsified oil spills, *Exp. Therm. Fluid Sci.* 28 (2004) 753–761. doi:10.1016/j.expthermflusci.2003.12.013.
 - [46] H. Kunieda, M.H. Uddin, H. Furukawa, A. Harashima, Phase Behavior of a Mixture of Poly(oxyethylene)–Poly(dimethylsiloxane) Copolymer and Nonionic Surfactant in Water, *Macromolecules*. 34 (2001) 9093–9099. doi:10.1021/ma011199i.
 - [47] United States Environmental Protection Agency, THICKSLICK 6535, Tech. Prod. Bull. #S-5. (2012). <https://www.epa.gov/emergency-response/thickslick-6535> (accessed October 2, 2019).
 - [48] United States Environmental Protection Agency, SILTECH OP-40, Tech. Prod. Bull. #S-6. (2012). <https://www.epa.gov/emergency-response/siltech-op-40> (accessed October 2, 2019).
 - [49] L. van Gelderen, N.L. Brogaard, M.X. Sørensen, J. Fritt-Rasmussen, A.S. Rangwala, G. Jomaas, Importance of the slick thickness for effective in-situ burning of crude oil, *Fire Saf. J.* 78 (2015) 1–9. doi:10.1016/j.firesaf.2015.07.005.
 - [50] L. van Gelderen, L.M.V. Malmquist, G. Jomaas, Vaporization order and burning efficiency of crude oils during in-situ burning on water, *Fuel*. 191 (2017) 528–537. doi:10.1016/j.fuel.2016.11.109.
 - [51] L. van Gelderen, J. Fritt-Rasmussen, G. Jomaas, Effectiveness of a chemical herder in association with in-situ burning of oil spills in ice-infested water, *Mar. Pollut. Bull.* (2016). doi:10.1016/j.marpolbul.2016.12.036.
 - [52] M. Afenyo, B. Veitch, F. Khan, A state-of-the-art review of fate and transport of oil spills in open and ice-covered water, *Ocean Eng.* 119 (2016) 233–248. doi:10.1016/j.oceaneng.2015.10.014.
 - [53] W.J. Lehr, R.J. Fraga, M.S. Belen, H.M. Cekirge, A new technique to estimate initial spill size using a modified fay-type spreading formula, *Mar. Pollut. Bull.* 15 (1984) 326–329. doi:10.1016/0025-326X(84)90488-0.
 - [54] J. Gros, D. Nabi, B. Würz, L.Y. Wick, C.P.D. Brussaard, J. Huisman, J.R. van der Meer, C.M. Reddy, J.S. Arey, First Day of an Oil Spill on the Open Sea: Early Mass Transfers of Hydrocarbons to Air and Water, *Environ. Sci. Technol.* 48 (2014) 9400–9411. <https://pubs.acs.org/doi/pdf/10.1021/es502437e?rand=c0udtyiz> (accessed September 12, 2019).
 - [55] J. Fritt-Rasmussen, P.J. Brandvik, A. Villumsen, E.H. Stenby, Comparing ignitability for in situ burning of oil spills for an asphaltenic, a waxy and a light crude oil as a function of weathering conditions under arctic conditions, *Cold Reg. Sci. Technol.* 72 (2012) 1–6. doi:10.1016/j.coldregions.2011.12.001.
 - [56] P.D. Panetta, R. Byrne, D. Hualong, The Direct Quantitative Measurement of in-situ Burn (ISB) Rate and Efficiency, in: *Int. Oil Spill Conf.*, 2017: pp. 1006–1019.
 - [57] W.D. Garrett, Confinement And Control Of Oil Pollution On Water With Monomolecular Surface Films, in: *Int. Oil Spill Conf. Proc.*, 1969: pp. 257–261. doi:10.7901/2169-3358-1969-1-257.
 - [58] W.D. Garrett, W.R. Barger, Factors Affecting the Use of Monomolecular Surface Films to Control Oil Pollution on Water, *Environ. Sci. Technol.* 4 (1970) 123–127. doi:10.1021/es60037a006.
 - [59] W.D. Garrett, W.R. Barger, Control and Confinement of Oil Pollution on Water with Monomolecular Surface Films., Washington, D.C., 1972. doi:AD-744943; NRL-MR-2451.

- [60] P. Pope, A.I. Allen, W.G. Nelson, Assessment of three surface collecting agents during temperature and arctic conditions, in: *Int. Oil Spill Conf.*, American Petroleum Institute, 1985: pp. 199–202. doi:<https://doi.org/10.7901/2169-3358-1985-1-199>.
- [61] Rijkwaterstaat, Shell Herder Trials, Report to the Dutch Ministry of Transport, Gravenhage, Holland, 1974.
- [62] S.L. Ross Environmental Research Ltd., Preliminary research on using oil herding surfactant to thicken oil slicks in broken ice conditions, Houston, Texas, 2004.
- [63] I. Buist, J. Morrison, Research on using oil herding surfactants to thicken oil slicks in pack ice for in situ burning, in: *28th Arct. Mar. Oilspill Progr. Tech. Semin.*, Calgary, AB, Canada, 2005: pp. 349–375.
<https://inis.iaea.org/search/searchsinglerecord.aspx?recordsFor=SingleRecord&RN=36103506>.
- [64] S. Potter, I. Buist, D. Cooper, S. Aggarwal, W. Schabel, J. Garron, R. Bullock, R. Perkins, P. Lane, Aerial Application of Herding Agents can Enhance In-Situ Burning in Partial Ice Cover, in: *Int. Oil Spill Conf.*, IOSC, Long Beach, CA, USA, 2017: pp. 2955–2975. doi:<https://doi.org/10.7901/2169-3358-2017.1.2955>.

APPENDIX A

Table A.1. – Detailed overview of the relevant small-scale laboratory to large-scale experiments with herding agents.

Year	Scale size	Oil type	Oil vol. [L]	Herder Type	Application	Water temp. [°C]	Air temp. [°C]	Salinity [‰]	Ice	Wind [m/s]	Wave	Remarks	Reference
1969	Buffalo River and Baltimore harbour	Jobo crude oil		Sorbitant esters (fatty acids) & polyoxyethylene alkyl ethers	Post	-	-	-	-	Yes	-	The monooleate surfactant achieved 5-10 mm slick thickness.	[57]
1970	Laboratory (feasibility study)			Dodecanol-1, Sorbitan monooleate, Oleyl alcohol, glyceryl trioleate, cottonseed oil, spreading oil and tricresyl phosphate.	-	-	-	-	-	-		Salinity does not have a large impact on various herders' capabilities.	[58]
1972	Laboratory tests and field test at the Chesapeake Bay			47 chemical surfactants	-	-	-	No/yes	-	-	-	The field test demonstrated the efficacy of the surfactants to confine the oil slick for various hours. The surfactant was periodically applied.	[59]
1974	Field tests in the North Sea (Rijkwaterstaat)		5200	Herding agent	-	Sea	Sea	Sea	-	-	-	The herder's thickening effectiveness lasted for 5 hours in open waters, winds of 6 m/s and 2 m seas. The herding agent was periodically replenished.	[60,61]
1985	Laboratory (1m ²) /pit at Prudhoe bay (60 m ²)	ANS	0.005 & 1000	Nalco 3WP-086, Corexit OC-5 and Shell's oil herder	Post	0 to 16 /0-2	-17 to 23/0-4	0 & 30	No	2-3	-	Good performance of herders in the field tests where 4-6 mm slick thickness was achieved. However, less than 1mm thickness was achieved by the herders on sheens.	[60]
2004	Laboratory (1m ²)	ANS, Chayvo, Pt. McIntyre & Northstar		EC9580	Post	0	NS	No	Yes	No	No	The herder was better in thickening in warmer water but was able to thicken all oils. However, sheen oils were poorly thickened.	[4]
2004	Laboratory	ANS		EC9580	-	0 & 20	-	Yes/No	Yes	No	No	The herding agent EC9580 resulted in more efficient at 25 than 0°C initially, but the performance was similar after one hour. The salinity does not affect the herder's effectiveness.	[62,63]
2005	Laboratory (1m ²)	ANS	0.001 & 1000	EC9580, OC-5 and USN (TS6535)	Post	0	-	0 & 35	Yes	No	No	The USN herder performed best over ANS crude oil. However, sheens did not perform well when were herded.	[4,21]
2005	Wind/wave tank in Laboratory (10 m ²)	ANS/ Cook Inlet, Gas Oil	1,2 & 5	USN (TS6535)	Post	0	-	35	Yes	Yes	Yes	The USN herder performed well in wind/wave and ice conditions and also performed well overnight.	[4,21,37]
		ANS	0.4 & 0.2		Post	0	-	35	Yes	No	No	Successful ignition and burning of the herded oil slick.	
	100 m ² basin at CRREL	Lubricant oil (Hydrocal 300)			Post	0	-21 & 0	Yes	Yes	No	Yes	The USN herded was effective in ice-infested waters and could thicken oil slick in the range 3-4mm. During herding, the oil slick broke due to wave action.	
2006	1000 m ² at Ohmsett	Blended Ewing Bank & Arab Medium (50:50)	20,22 & 60	USN (TS6535)	Post	0	-	Yes	Yes	Yes	Yes	The USN herded generally performed well, but as the wind increased, its capability decreased (more than 2 m/s).	
2006	24 m ² water pool at the Fire Training group in Prudhoe Bay	Kuparuk	7.5 & 15	USN (TS6535)	Pre & Post		-17	Yes	-	Yes	Yes	The USN herder was effective with ice presence (up to 30%), longer non-breaking waves did not break the slick, and ignition was achieved successfully.	[4,20,21]

2008	Small water basin (1m ²) and in a tray (0.08 m ²)	Statfjord & Heidrun		USN (TS6535)	-	-	-	15 & 30	Yes	No	-	The USN herder performed better over Heidrun crude oil.	[4,19]
	Field tests in the Barents Sea	Heidrun	102 640	USN (TS6535)	Pre Post	~0	~0	Sea	-	5-5.5 4.4	-	The herded oil slick ignited and burnt successfully.	
2009	Dynamic tray (0.05 m ²) and water basin (1 m ²)	ANS, Chayvo & Diesel fuel oil	0.005 & 0.05	OC-5, USN (TS6535) and Flurosurfactant PolyFox PF151N	Post	0	0-20	0 & 35	No	No	No	The Polyfox herder performed best at 20 °C, whereas the USN herder performed best at 0°C. Poor performance was observed over the Chayvo crude oil.	[29]
	1 m ²	ANS, Kuparuk, and evaporated ANS	1	Silicone-based herders: Sylgard 309, Silsurf A004-UP (OP40), Silube J208-912 and Siltech C-404	Post	0	0-20	0, 15 & 35	No	No	No	The Silfurf A004-UP (OP40) herder proved to be the best but decline after one hour. All herders performed better in fresh water, and in evaporated crude. The herding agents performed better on Kuparuk than ANS.	
	10 m ² wind/wave tank		2	PF-151N and an A004-UP (OP40)				35	Yes			The herder OP40 was better than PF-151N. Both herders maintained their herding capabilities for over one hour. The presence of ice block reduced the herders' effectiveness slightly.	
	1 m ²	Kuparuk	1	Silsurf A004-D, Silsurf A108, and Siltech B2-P3-A50,	Post	0	-	35	Yes	No	No	All new silicone herders performed better than TS6535 and Silsurf A004-UP (OP40).	
	100 m ² basin at CRREL	Kuparuk	7.5 & 15	Silsurf A004-D and Silsurf A108	Post	0	-		Yes			Both herders performed better than USN (TS6535) in a previous experiment [20], except for 30% ice coverage. The herder Silsurf A108 performed better than Silsurf A004-D.	
2015	Lab	ANS, evaporated ANS (at 23% and 31%)	0.5	OP40 & TS6535	Post	0	-	0 & 35	-	-	-	The herder OP40 performed better than TS6535 on fresh ANS. However, on evaporated ANS, OP40 had similar effects as TS6535. The exception was on a 31% evaporated ANS, where TS6535 outperformed OP40 in saline water. TS6535 performed better in fresh water.	[30]
	1800 m ² water basin at the Poker Flat Research Range, University of Alaska Fairbanks, Fairbanks AK	ANS	70,75,15 & 155			0	-7 to 15		No	1-3.3	No	Both herders performed well over the free-floating oil slick. A helicopter was used to apply the herder. Successful ignition and burning were achieved in some of the trials.	[10,14,30,64]
2017	Laboratory apparatus (Ø 0.38 m)	ANS	0.05& 0.1	OP40	Post	1	0 to -13	0	Yes	<1.5	No	The herder OP40 demonstrated to thicken the oil slick in presence of ice. Successful burning was achieved.	[10]
	9 m ² water basin		3.8 & 4.5	OP40									
2017	Dynamic tray (0.05 m ²)	Fresh and weathered ANS, Grane and Terra Nova	0.05	OP40 & TS6535	Post	0	-	35	No	No	-	Across all experiments in the various experimental apparatuses , both herders could effectively thicken the studied crude oils. Both herders resulted in thicker thickness over evaporated and emulsified crude oils than over their fresh counterparts. However, both herders' thickening effectiveness over the emulsions with high water content showed decay in some cases in the small-scale experimental apparatuses . Only in the mid-scale experimental apparatus (28.5 m ²), TS6535 resulted in very poor performance over the weathered ANS. The presence of slush ice (up to 30% ice coverage) in the water decreased the performance of both herders. Successful ignition and burning were achieved over herded ANS and Grane with both herders.	[31]
	1 m ²	Fresh and weathered ANS, Grane, Endicott, and Terra Nova	0.5	OP40 & TS6535	Post	0	-	35	Yes	No	No		
	10 m ²	Fresh and weathered ANS and Grane	1	OP40 & TS6535	Post	0	-	35	Yes	No	No		
	10 m ² wind/wave tank	Fresh and weathered ANS and Grane	0.5	OP40 & TS6535	Post	0	-	35	Yes	No	Yes		
	28.5 m ²	Fresh and weathered ANS	7.5	OP40 & TS6535	Post	0	-4	35	Yes	No	No		
2017	Lab cell (1m ²)	DUC	0.1 to 0.24	OP40	Post	3-8	-	0	Yes	No	No	The herder OP40 could achieve oil slick thickness in excess of 3mm even in the presence of ice. The fracturing of oil slicks was observed with the presence of ice, especially when there was a large presence of ice blocks. Successful ignition and burning were achieved only on the large herded oil slick-lets.	[51]
	Mid-scale tank (19 m ²)		3.1-15			6-12	-	0	Yes	0-6	No		
2017	1 m ²	Grane, Statfjord & evaporated Statfjord	0.5	TS6535	Post	12	-	35	No	No	No	The herder TS6535 showed better performance on fresh Grane than on fresh and evaporated Statfjord crude oils.	[32]

2017	Frigg Field, North Sea (Norway)	Grane	6000 & 4000	TS6535	Post	>10	>10	Sea	No	3-5	Yes	The herder could thicken the oil slick in calm conditions (3-5 mm thickness) in winds up to 5 m/s. There were difficulties in applying herder from the boat; therefore parts of the oil slick were not herded. The burning of the herded oil was affected by the high winds.	[32,38]
2018	Lab cell (1 m ²)	Degassed Kashagan oil & Buzachi oil	0.1	OP40 & TS6535	Post	5 & 15	-	6, 12 & 18	-	No	No	Both heders achieved a minimum ignitable thickness. However, OP40 was more effective than TS6535. Salinity does not have an impact. Thickening efficiency increases with water temperature. Both herders are more efficient in the heavier crude oil (Buzachi).	[34]
2018	Lab cell (1 m ²)	Agbami, Hibernia, Anadarko, ANS, Ewing bank, Endicott, Apline, IFO 120, Doba Chad, Rock, Platform Gina H14, Platform Gina (fresh), Harmony, Canadian Sour		OP40 & TS6535	Post	4 & 20	No	Yes	No	No	No	TS6535 was initially less efficient than OP40, however, over time TS6535 maintained the same thickness for longer times. On the contrary, OP40 showed rapid decay.	[35]
2019	Lab cell (1 m ²)	Grane, evaporated Siri, evaporated Oseberg blend & weathered Oseberg blend	1.6 – 25	OP40	Pre & post	5-18	2 – 28	32	No	0.2 – 4.9	No	The herder OP40 successfully thickened all fresh. The herder's thickening capabilities were found to be a function of the oil type and weathering degree of the oil.	[33]

APPENDIX B

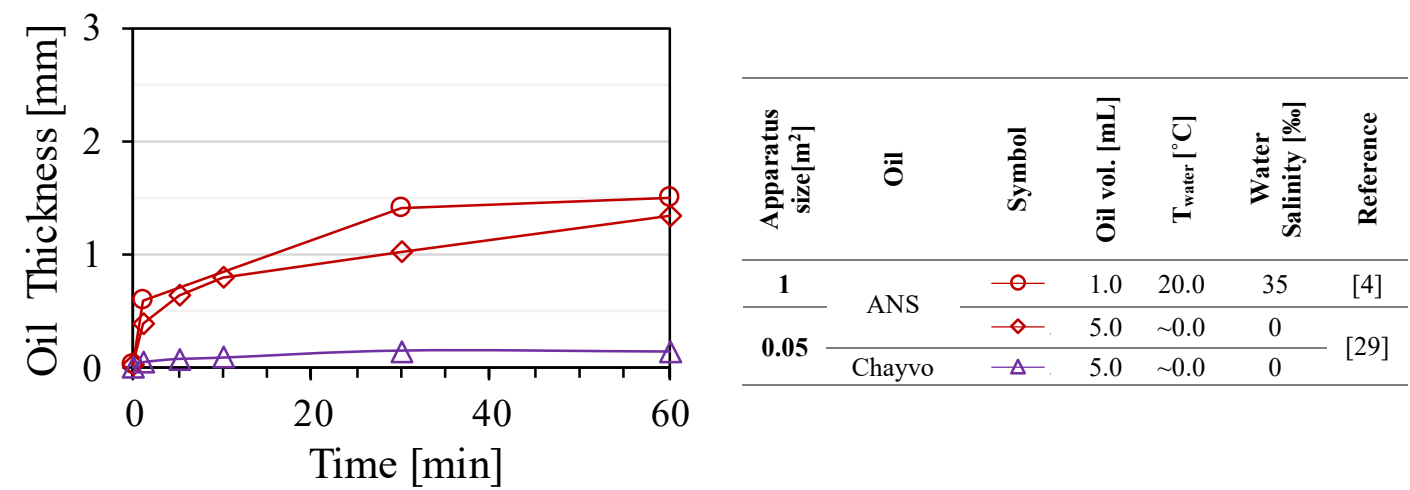


Figure B. 1 – Oil thickness results as a function of time from two studies where sheens of ANS and Chayvo crude oils were herded with TS6535. Data were obtained from [4,29]. The plotted lines are just for visualization.

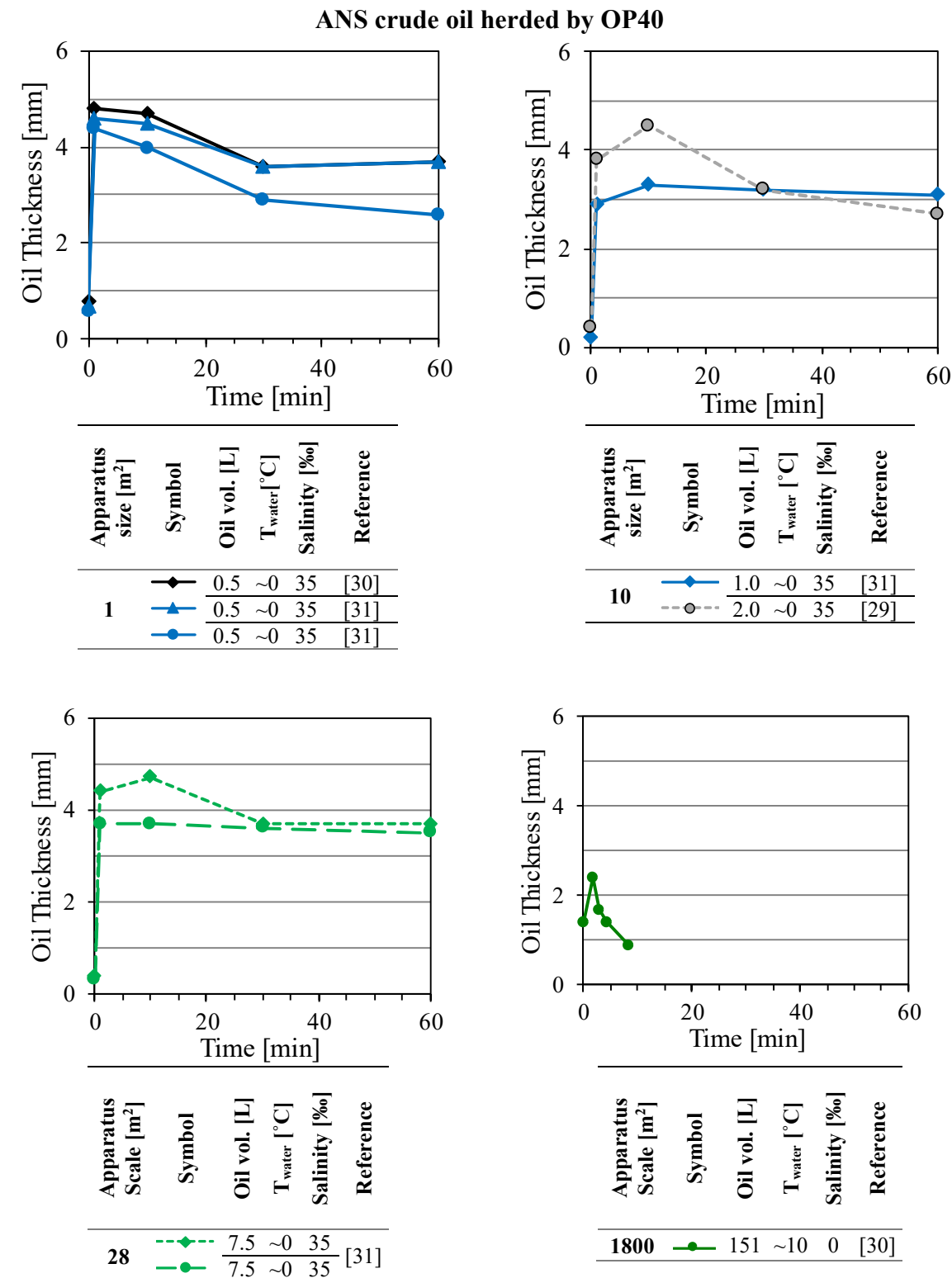


Figure B. 2 – Oil thickness over time from various studies where ANS crude oil was herded with OP40. The selected data is classified according to the rig scale, volumetric size and water temperature. Data is from [29–31].

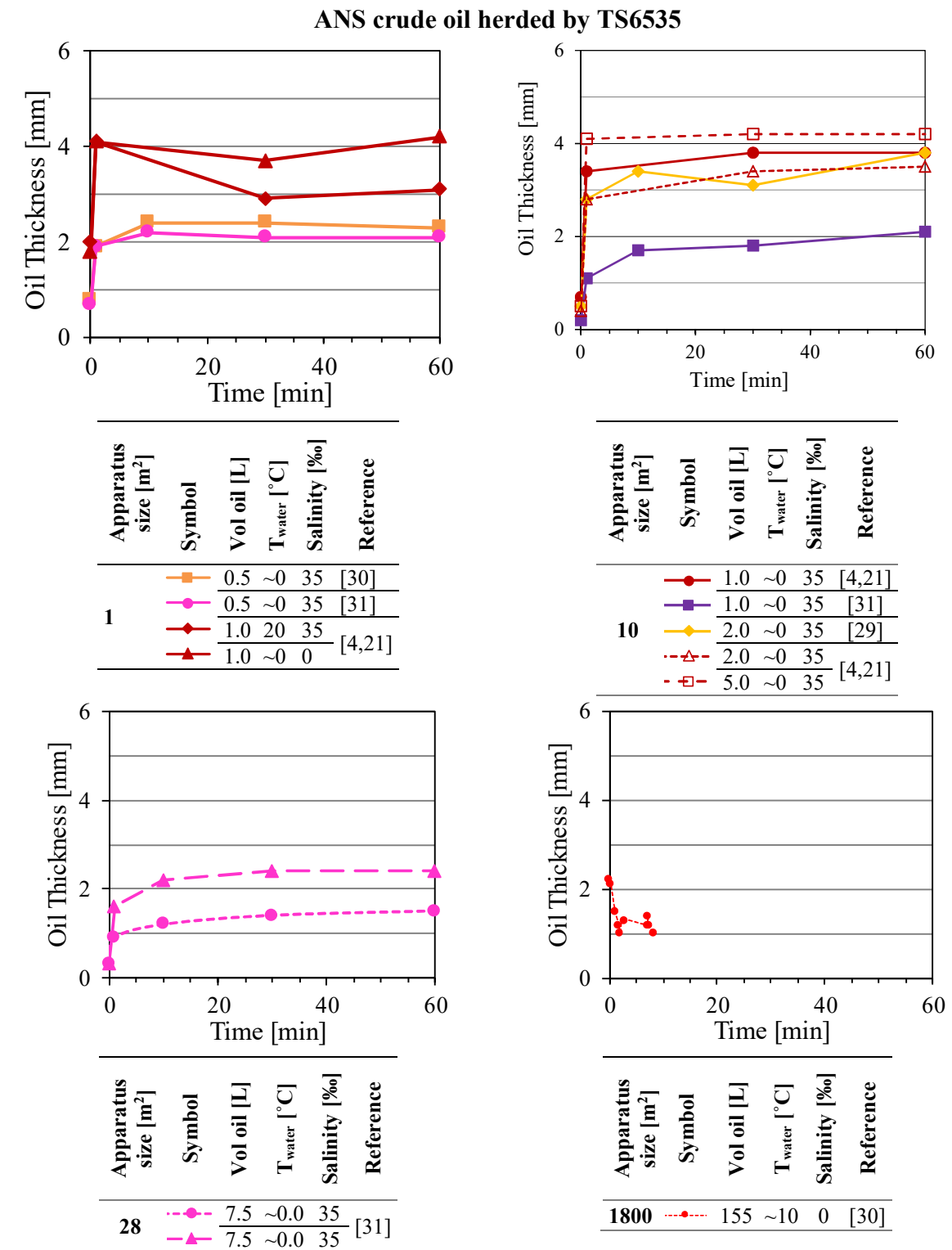


Figure B. 3 – Oil thickness results over time from various studies where ANS crude oil was herded with TS6535. The selected data is classified according to the rig scale, volumetric size, and water temperature. Data is from [4,21,29–31].

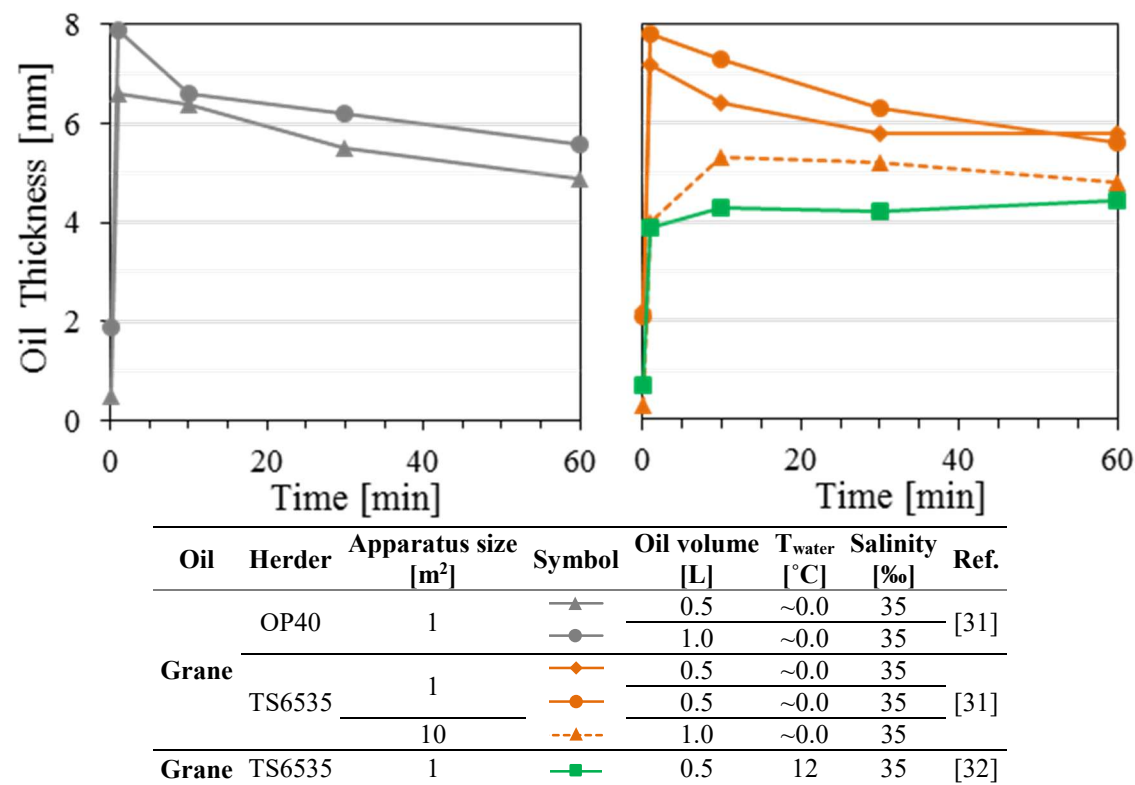


Figure B. 4 – Oil thickness results over time from various studies where Grane and Grane blend crude oils were herded with OP40 (left pane) and TS6535 (right pane). The selected data is classified according to the rig scale, volumetric size and water temperature. The experimental conditions are similar in water temperature and water salinity. Data is from [31,32].

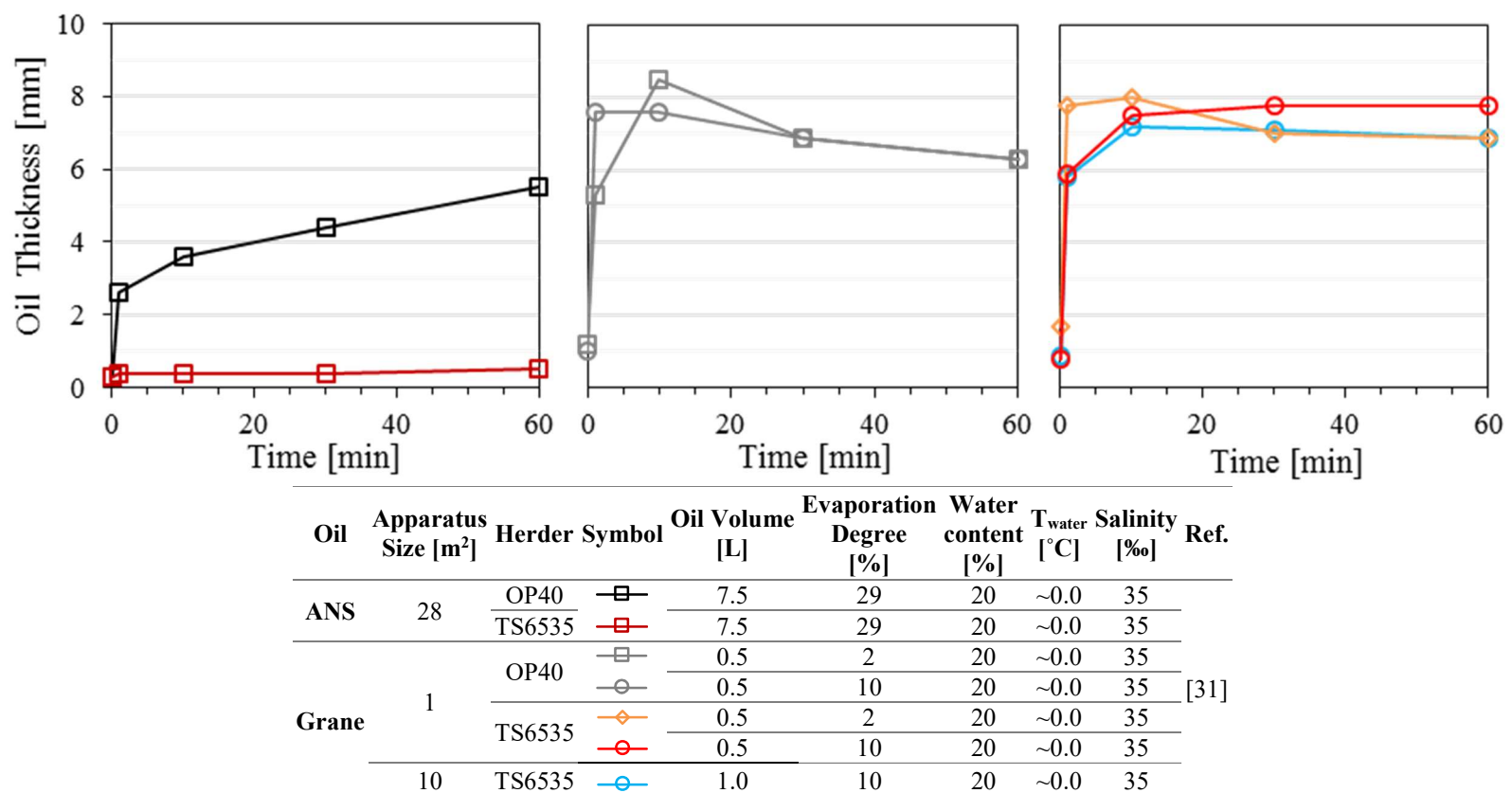


Figure B. 5 – Oil thickness results over time from a study where weathered Grane and ANS crude oils were herded with TS6535 and OP40. Data is from [31].

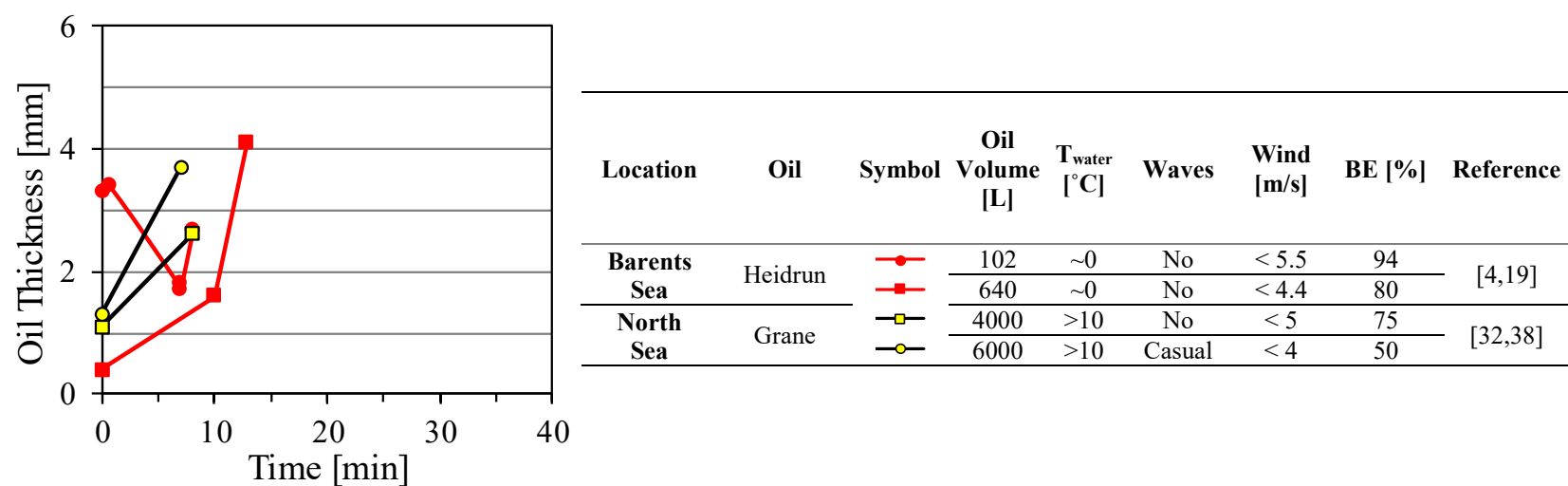


Figure B. 6 – Oil thickness results over time from field experiments where Heidrun and Grane crude oils were herded with TS6535. Data is from [4,19,32,38].

APPENDIX C

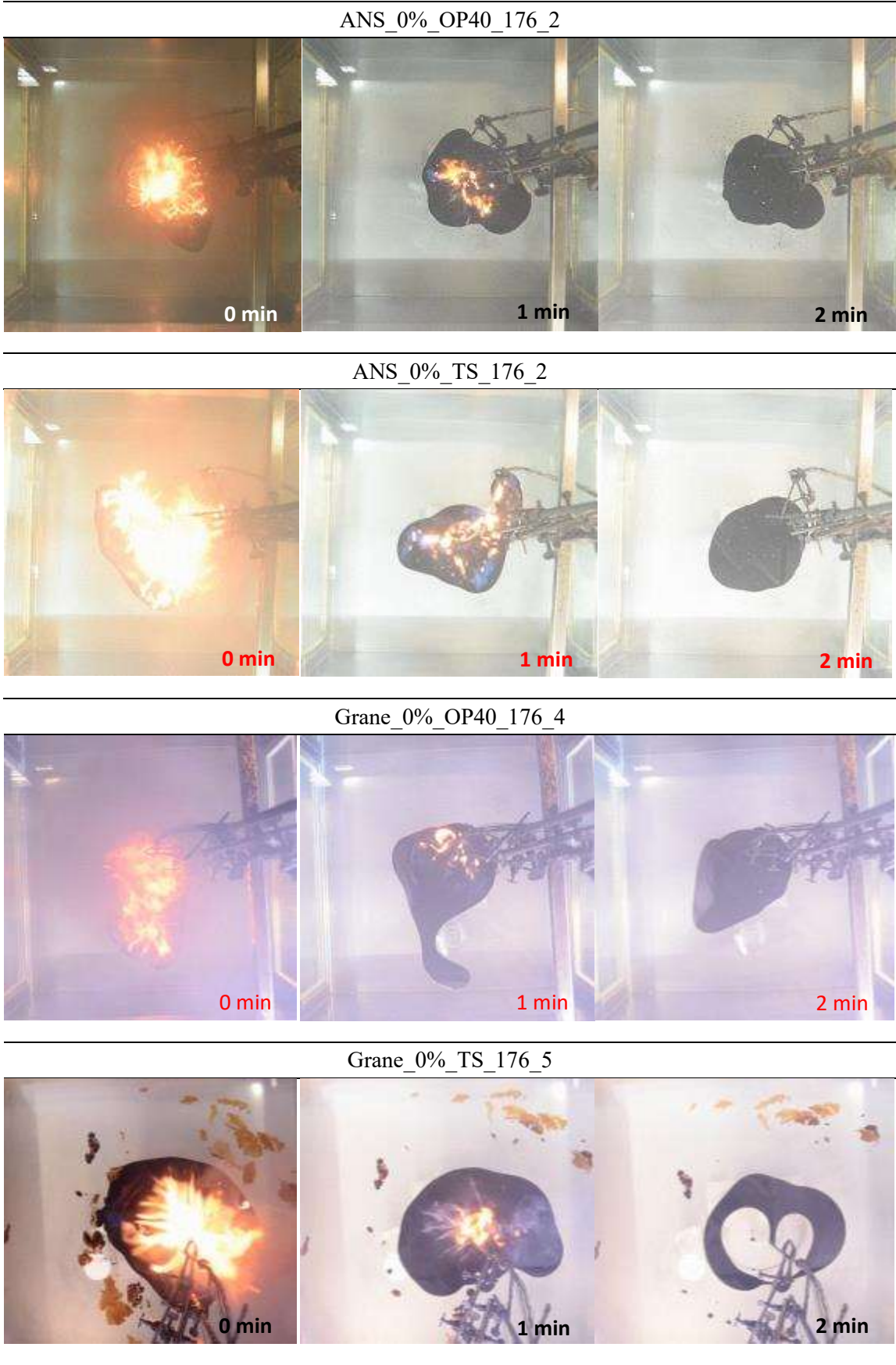


Figure C. 1 – Sequence of images during burning of ANS and Grane crude oils.